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THEORY AND APPLICATIONS OF CHEMICAL AND RADIOACTIVE TRACERS

J. BIGU

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ELLIOT LAKE LABORATORY

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THEORY AND APPLICATIONS OF CHEMICAL AND RADIOACTIVE TRACERS

J. Bigu*

ABSTRACT

The theory and applications of chemical and radioactive gaseous tracers were examined with particular emphasis on their use in ventilation studies in underground uranium mines. A number of specific examples of practical interest to AECB inspectors are given as well as the methodology and techniques recommended in each case to determine the ventilation variables of interest. In addition, a variety of detectors and detection systems in common use in tracer gas work are reviewed. Finally, a computer based, portable, gas chromatograph using an electron capture detector suitable for SF_6 (a common tracer gas in ventilation studies) is described. This instrument will be used in field studies to be conducted in several underground uranium mines, shortly.

Key words: Tracer techniques; Ventilation studies; Gas chromatography.

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THÉORIE ET APPLICATION DES TRACEURS RADIOACTIFS ET CHIMIQUES

J. Bigu*

RÉSUMÉ

On a réalisé une étude de la théorie et des applications des traceurs gazeux chimiques et radioactifs et en particulier de leur utilisation pour le contrôle de l'aérage des mines d'uranium souterraines. Des exemples spécifiques d'un grand intérêt pour les inspecteurs de la Commission de contrôle de l'énergie atomique (CCEA) sont présentés, de même que la méthodologie et les techniques recommandées dans chaque cas particulier pour déterminer les variables de l'aérage qui présentent de l'intérêt. De plus, un certain nombre de détecteurs et de systèmes de détection couramment utilisés dans les travaux exécutés au moyen de gaz traceurs sont passés en revue. Enfin, on donne une description d'un chromatographe en phase gazeuse assisté par ordinateur, portatif et doté d'un détecteur à capture d'électrons adapté au SF_6 (gaz traceur couramment employé dans les études de l'aérage). L'appareil sera en service au cours d'études sur le terrain qui seront menées sous peu dans plusieurs mines d'uranium souterraines.

Mots clés : méthodes analytiques au moyen de traceurs; études de l'aérage; chromatographie en phase gazeuse.

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INTRODUCTION

One of the most common methods of controlling airborne pollutants is by forced mechanical ventilation. The intelligent use of such a control method requires an efficiency test of the ventilation system in order to determine such important variables as airflow, air residence time, and air recirculation characteristics of the ventilation air at the location of interest.

Ventilation systems are extensively used in industrial, commercial and residential buildings, research, military and sports installations, medical and laboratory facilities, factories, and underground mines and mills, among other places and locations.

The study of mine air ventilation patterns and airflow conditions in underground mines and mills can be time consuming, labour intensive and very tedious. Smoke tubes provide only rough approximations of air flow direction and velocity whereas anemometry, although capable of accurately measuring air velocity, presents some practical problems for large-scale airflow determinations because airflows can only be determined approximately.

The problems inherent to smoke tubes and anemometers can be minimized or altogether eliminated by using tracer gases which make possible the accurate determination of both airflow patterns throughout the mine or mill, and the average mine air velocity over large distances.

The most frequent application of tracer gases in recent years has been in the evaluation of ventilation systems in industrial plants, homes, buildings, laboratory facilities, and in underground mines. Tracer gas studies have also been carried out to determine atmospheric dispersion of gaseous chemical pollutants released, from pollutant sources, into the environment. A few studies have used tracer gases to determine dispersion phenomena in large gas lines, adsorption equilibria in complex chemical

situations, and mechanisms in 'fluidized' bed reactors. In underground mines, studies have been conducted to assess overall and local ventilation, to determine leakage through mine stoppings, and to identify recirculation paths.

The most common application of tracer gases is in determining air exchange rates, air infiltration and leakage, and to assess ventilation efficiency.

Tracer gases can essentially be of two kinds, namely, 'chemical' gases and radioactive gases. In general, the tracer gas to be used in a working environment must have a number of special properties such as:

a) It must be non-toxic so it presents no pontential biological or physiological hazards to personnel exposed to the gas even at relatively high concentrations at which it may occasionally be released;

b) It should be easily detectable, even at low concentrations;

c) It should present little difficulty for accurate analysis and interpretation of experimental data;

d) It should be chemically inert so that it does not react with other chemical species in the environment which may affect its physico-chemical properties;

e) It must be thermally stable so that it does not decompose or disassociate, forming unwanted, and/or potentially toxic or useless chemical by-products;

f) It must not occur naturally, or if it does, not in sufficient quantities to interfere or mask field observations in the working environment of interest;

g) It should be insoluble in water and it must not be adsorbed on the surface of any materials likely to be encountered in, say, underground mines, for example;

h) It must not be absorbed by materials encountered in the experimental

sites:

i) Its density should be similar to that of air so that good mixing takes place and the sample does not 'sink' by gravity or 'float' above the air mass; and

j) It should be cheap and easy enough to handle for extensive routine applications.

Although item f) is often recognized as a prerequisite that a tracer gas must have for practical applications, it will be shown that this is not strictly necessary or desirable. In fact, some naturally-occurring airborne radionuclides (e.g., radon, thoron, and their respective progeny) can be used in some special cases and under certain experimental conditions as useful indicators of the dynamic characteristics of airflow in underground environments (1-3).

A wide variety of tracer gases has been used in the past, such as H_2, O_3, CO_2, N_2O, CH_4, C_3H_8, SF_6, and a number of Freons, i.e., fluorocarbons. Some of these tracers have been in common use since 1958 or before.

However, among the chemical tracers, sulphur hexafluoride (SF_6) is the gas most widely used because it can be synthesized easily, and because it meets all the requirements listed above. Sulphur hexafluoride and fluorocarbons are chemical compounds that can easily be detected and quantified by means of conventional gas chromatographs using gas detectors of the electron capture type. Table 1 shows some of the properties of SF_6.

Other potentially useful chemical compounds that could be used as tracer gases for the same purpose as that of interest here (provided these gases satisfy the conditions indicated in items a) to j)) may require other identification and quantification techniques or detectors such as infrared (IR), spectroscopy (e.g., CO_2, CH_4, C_3H_8), thermal conductivity, flame photometry or flame ionization detectors to name but a few detectors. A

description of these detectors and their mode of operation will be presented below.

Radioactive tracer gases are, unlike chemical tracer gases, unstable, i.e., they transform into other isotopic species by radioactive decay. Hence, the radioactive half-life of the radioactive tracer gas chosen must be suitable and compatible for practical applications. One special useful feature of some radioactive tracer gases is that the radiation emitted in their decay is penetrating enough to permit its detection through metal and plastic pipes, and ventilation ducting.

This report examines primarily the use of chemical tracer gases in underground uranium mines and uranium mills in order to determine airflow patterns and ventilation conditions, particularly regarding air recirculation and other important airflow conditions of practical interest. Furthermore, the uses of radioactive tracer gases such as ^{85}Kr, ^{41}Ar, ^{133}Xe, and ^{79}Kr (4-8), and naturally-occurring airborne radioactive elements such as radon (^{222}Rn) and thoron (^{220}Rn), and their progeny to mine ventilation studies are also examined.

EXPERIMENTAL APPARATUSES - GAS CHROMATOGRAPHY

The use of tracer gases for ventilation studies requires instrumentation suitable for tracer gas identification and quantification. For non-radioactive tracer gases and gaseous and volatile chemical compounds, use is made of gas chromatography. Although the word implies colour, there is no direct connection except that the first compounds that were separated by this technique were coloured plant pigments.

As previously indicated, techniques other than gas chromatography can be used effectively to investigate ventilation conditions in working and living environments. These techniques include the use of naturally-occurring

and man-made radioactive tracers, gaseous or airborne. The methods and techniques used for radioactive airborne tracers will be discussed in a later section of this report.

Chromatography can be defined as that technique for the separation, identification and quantification of a mixture of solutes in which separation is brought about by the differential movement of the individual solutes through a porous medium under the influence of a moving solvent. Tswett, a Russian biologist, was probably the first person (as long ago as 1906) to realize the potential of such a technique. His studies were probably the first ones to demonstrate adsorption column chromatography (cited in ref. 9). However, it was not until Martin and Synge introduced partition chromatography that Tswett's work ceased to be a laboratory curiosity. Consden, Gordon and Martin (1944) described paper chromatography, a technique in which separations are attained on sheets of filter paper, mainly by partition. Two further important developments followed, namely, thin layer chromatography (ca 1940), a technique fully standardized by Stahl (1958), and gas chromatography (Martin and James, 1952). (Note: the above citations have been taken from ref. 9. See also (10)).

GAS CHROMATOGRAPHY

Gas chromatography is a technique designed for the separation, identification, and quantification of gases and volatile liquids and solids in the gaseous state.

Gas chromatography operates as follows. A sample of the material or mixture of compounds to be examined is injected into a stream of an inert gas (i.e., inert gas carrier) such as nitrogen (N_2), hydrogen (H_2), carbon dioxide (CO_2), helium (He), or argon (Ar) which carries it into a column containing a suitable medium capable of retarding the flow, by varying degrees, of the individual components of the sample as they flow through the 'separation'

column. The separated components of the mixture then emerge from the column at discrete intervals, which are characteristic of each component, and pass through a suitable detector. Differences in adsorption or partition on the material in the column is what makes separation of the different compounds in the gaseous mixture possible. As a general rule, gas analyses are carried out on adsorption columns (gas/liquid chromatography), whereas liquids and volatile solids are separated on partition columns (gas/liquid chromatography).

The adsorption (separation) column of a gas chromatograph usually consists of a coil of metal or glass tubing stuffed with a solid support coated or impregnated with a suitable adsorbing liquid. The correct column for any separation depends primarily on the kind and amount of adsorbing liquid and the type and mesh of the solid support. There is a great variety of materials to choose from depending on specific applications. For this reason, the reader is advised to consult the gas chromatograph manufacturers and the manufacturers of gas chromatography specialties for materials of common use in particular applications. (Note: in some cases capillaries are used instead of adsorbing columns.)

After the chemical gaseous mixture of interest has been separated in the column, the different chemical species enter the detector(s) where they are identified and measured. A signal is produced in the detector, which in most cases is subsequently amplified and further processed and finally recorded by means of a strip chart recorder, a cathode ray tube (CRT), or a printer. The more advanced chromatographs are computer-based, and the data obtained can be stored on floppy discs or on a hard core disc, and displayed on command.

Depending on the gaseous compound(s) to be separated and identified, gas chromatographs can make use of a variety of different detectors. Some of

the detectors in most common use are of the following types:

1. Thermal conductivity,
2. Flame ionization,
3. Photoionization,
4. Argon ionization,
5. Flame photometric,
6. Electron capture, and
7. Other detectors not listed above.

1. Thermal Conductivity Detectors (TCD)

The operation of this type of detector depends on the fact that heat flows away from a hot body at a rate dependent on the composition of the gas surrounding the body. The transport of heat between the body and the surrounding gas, i.e., the heat conductivity, depends on the rate of motion of the gas molecules and, hence, on their molecular weight. For this reason, faster cooling rates occur with smaller gas molecules because of their higher mobility.

Typical thermal conductivity detectors consist of a double arrangement of thermistors, platinum wires, or metal alloy wires, one in a pure carrier gas stream (e.g., He) and the other in the column effluent stream. The wires (or thermistors) form part of a Wheatstone bridge. A change in column effluent composition is reflected in a heating of the wire compared with the wire in the standard, i.e., carrier gas. The heating of the wire changes its electrical resistance causing an electrical imbalance in the Wheatstone bridge which is measured by the recorder of the gas chromatograph. The heat increase in the 'test' wire relative to the wire immersed in the carrier gas can easily be understood if He is used, as the molecular size of this carrier is very small, usually smaller than many other gas molecules, thereby providing maximum cooling (heat transport) effects.

Although thermal conductivity detectors respond to all substances they find special use in the detection of water vapour.

2. Flame Ionization Detectors (FID)

In this type of detector, hydrogen (H_2) is mixed with air and the organic compound(s) to be analyzed. The carrier gas is helium (He) or nitrogen (N_2). The mixture is ignited and the flame produced burns H_2 and air to produce water (H_2O), and also produces carbon dioxide (CO_2) from the burning of the organic compound(s). The CO_2 molecules are ionized to give ions in the detector and the amount of these ions is subsequently measured and amplified. The chemical compound carbon disulphide (CS_2) is not detected by flame ionization detectors. For this reason, standard solutions in CS_2 are often used for both quantitative and qualitative work. The response of flame ionization detectors (FID) to materials is linear, thereby making FIDs specially suitable for quantitative work. The main application of flame ionization detectors is in the separation and analysis of organic compounds.

3. Photoionization Detectors (PID)

The photoionization detector operates on the principle of ionization of organic chemical compounds by ultraviolet (UV) radiation of energy equal to or greater than the ionization potential (IP) of the species. The principle of photoionization is illustrated below.

$$R + h\nu \rightarrow R^+ + e^-$$

where R^+ is the ionized species and $h\nu$ is a photon of UV light of frequency ν. Ultraviolet light is produced by specially designed lamps which generate UV light of energy up to 11.8 eV, which is sufficient to detect most organic compounds. (The IP corresponding to organic molecules is in the range 8 to 11.5 eV.)

Photoionization detectors consist of two components:

1. An interchangeable UV source which emits a selected energy 'line' and

ionizes organic chemical species with IPs $\leq$ the energy of the UV source:

2. An ionization chamber where the ionization process takes place and the ion current produced, which is proportional to the ion concentration, is measured.

The carrier gas used in PIDs is helium (He).

4. Argon Ionization Detectors (AID)

This type of detector is suitable for the detection of most organic compounds. Although for some compounds the sensitivity of AIDs may be less than the sensitivity of flame ionization detectors (FIDs), their simplicity and ruggedness make them ideally suitable for field and portable use.

The principle of operation of the argon (Ar) ionization detector is based on the excitation of argon atoms by a β-source such as tritium (^3H) according to:

$$Ar + \beta \rightarrow Ar^* + Ar^+ + e^-$$

where β indicates an excited state of argon (exciton). When argon flows over a ^3H source, Ar^* and argon ions (Ar^+) are formed. The excitation energy of Ar is ~11.6 eV. Hence, when Ar enters a detector containing ^3H, a steady-state of Ar^* is developed.

When organic molecules are introduced to the detector they collide with the excited argon atoms (Ar^*) and, since the IP of organic molecules is in the range 9-11 eV, the collisions result in energy transfer (~11.6 eV) from Ar^* to the organic species by de-excitation of the argon atoms, and subsequent ionization of the organic species (R) according to:

$$Ar^* + R \rightarrow Ar + R^+ + e^-$$

The above reaction produces positive and negative charges in the detector cell and, if a high voltage is supplied to the detector, an increase in current develops which can subsequently be amplified and measured.

5. Flame Photometric Detectors (FPD)

Flame Photometric Detectors are designed for ambient level measurements of sulphur compounds (e.g., SO_2, H_2S, COS, and mercaptans) and phosphorus compounds (e.g., PH_3). The gas chromatographic column provides the separation necessary to eliminate the potential interference of similar chemical compounds which may be found in the sample. The carrier gas, which transports the sample through the column, is mixed with air and is burned in a hydrogen rich flame. The decomposition of the sample components in this flame gives a characteristic optical emission which is filtered and then detected by a photomultiplier tube. Selective detection of either sulphur or phosphorus compounds is done by choosing the appropriate optical filter.

6. Electron Capture Detectors (ECD)

The electron capture detector is a highly sensitive detector with a great selectivity to compounds capable of capturing electrons.

The principle of operation of electron capture detectors is as follows. When a gas carrier such as argon (Ar) flows over a pure β-emitter such as ^{3}H or ^{63}Ni placed between two parallel plates (to which an electrical potential is applied), the following reaction takes place:

$$Ar + \beta \rightarrow Ar^{+} + e^{-}$$

If now a chemical compound, R, that has affinity for electrons is mixed with the gas carrier, the following reaction develops:

$$R + Ar^{+} + e^{-} \rightarrow R^{-} + Ar^{+}$$

Hence, the light, fast moving electron is attached to R forming a large, slow moving negative ion (R^{-}). Because of the low voltage supplied to the detector, i.e., β-source/parallel plate arrangement, the ion mobility is decreased with the resultant decrease in negative charge. A negative signal develops that can be amplified and measured.

Electron capture detectors are particularly suitable for the detection

of halocarbons, i.e., halogenated compounds such as fluorocarbons, and hence, finds special application in the detection of SF_6 in ventilation studies.

7. Other Special Detectors

There are a number of other, highly specialized, gas chromatograph detectors for special applications such as Electrolytic Conductivity Detectors (El. Con. D), Nitrogen-Phosphorus Detectors (NPD), and Far Ultraviolet Absorbance Detectors (FUVAD), among others.

The El. Con. D is used extensively in identification and quantification of PCBs, pesticides, herbicides, and other organic compounds containing nitrogen and chlorine by reducing them to NH_3 or HCl, and measuring the conductivity changes which result when these gases are absorbed in deionized water. This detector is also quite sensitive to purgeable halocarbons.

The NPD is a flame ionization detector which uses an electronically controlled rubidium bead. The selectivity for nitrogen with respect to carbon is greater than 10^4:1. This type of detector is ideal for drug analyses requiring the use of open tubular columns.

The principle of operation of the FUVAD involves measurement of the attenuation of far UV photons by molecules passing through a special cell housing a photodiode sensitive to far UV radiation. The changes in UV photon flux exhibit a Beer's Law relationship with molecular species concentration. Responses are predictable as a function of the molar extintion coefficient. Absorbance measurements are conducted in the 120-150 nm region. The detector is of the non-destructive type and can, therefore, be used in series with other detectors. The FUVAD is used in the detection of hydrocarbons.

There are other types of detectors, e.g., hot wire detector, ion-trap detectors, among others, which will not be described here for the sake of time, space and simplicity.

The experimental apparatus which will be used in a field investigation

to determine the usefulness and practicality of employing tracer gas techniques to evaluate ventilation conditions in underground uranium mines and uranium mills by AECB Inspectors, will be described in some detail in the Appendix.

THEORETICAL BACKGROUND

When tracer gas is released at a constant rate, S, into a volume, V, ventilated at an airflow rate, Q, the rate of change of the tracer gas concentration in V, say C, can be represented by the following differential equation:

$$\frac{dC}{dt} = -(\frac{Q}{V})C + S \qquad \text{Eq 1}$$

where C is given in, say, tracer gas molecules per unit volume (mol/m^3) and the production rate S is given in gas molecules per unit volume per unit time (mol/m^3s).

The first term on the right hand side of Equation 1 represents the removal of tracer gas by the flow of air, whereas S is, as defined above, the production rate of gas within V.

The solution to Equation 1, subject to the boundary condition C(t=0) = 0, is:

$$C(t) = (S/\tau)\ (1-e^{-\tau t}) \qquad \text{Eq 2}$$

where, $\tau = Q/V$.

Equation 2 shows that for sufficiently long times, C(t) reaches a constant, steady-state value of S/τ.

When the source of tracer gas is removed from V, the gas concentration in the volume of interest can be described by Equation 1 with S=0. Solving this equation, subject to the boundary condition $C(t=0) = C_o$, gives:

$$C(t) = C_o\ e^{-\tau t} \qquad \text{Eq 3}$$

Equations 2 and 3 have been derived under the assumption of perfect mixing of tracer gas with air in V. In actual practice, perfect mixing is an idealized situation which rarely occurs. The above equation can be modified to take into account imperfect mixing by introducing a 'mixing' factor, k, into the first term on the right hand side of Equation 1, i.e., substituting τC by $k\tau C$, and hence, τ (in Equations 2 and 3) by $k\tau$.

Equation 3 can be rewritten in a slightly different form, namely:

$$\ln(C(t)/C_o) = -\tau t \qquad \text{Eq 4}$$

If $\ln(C(t)/C_o)$ is plotted against t (elapsed time), the slope of the line represents τ, i.e., the number of air changes in V per unit time.

Equation 3 shows, as expected, that C(t) reduces to zero at sufficiently long times. The time elapsed for C(t) to reach a constant value in the gas build-up case (see Equation 2), and 0 in the gas decay case (see Equation 3) depends on τ, and can be calculated easily from values of Q and V.

Because of the finite time response of the detector to a tracer gas (radioactive or non-radioactive), Equations 2 and 3 are important in understanding the shapes of the curves C(t) versus t recorded by, say, a gas chromatograph or a nuclear detector.

It is important to relate the amount of tracer gas released at a given point by the source, e.g., a gas bottle or container of some kind containing the tracer gas) and the amount of the (released) tracer gas actually reaching another, arbitrary, point where a suitable tracer gas detector (e.g., a gas chromatograph or GC, for short) has been located for monitoring purposes. Because of leakage, splitting, and other reasons, usually not all the tracer gas released by the source reaches the monitoring station. Hence, the following expression can be written:

$$V_D = \delta V_s \qquad \text{Eq 5}$$

where V_D and V_s are, respectively, the volume of tracer gas detected and

released. The symbol $\delta(<1)$ represents an efficiency or recovery factor.

It is not difficult to see that for a single, continuous, tracer gas release (11)

$$V_D = Q\int C(t)\,dt \qquad \text{Eq 6}$$

If the tracer gas release extends over a period ΔT long enough so that an average concentration can be accurately estimated, one can write:

$$\bar{C} = \int C(t)\,dt/\Delta T \qquad \text{Eq 7}$$

Hence, Equation 6 becomes:

$$V_D = Q\,\bar{C}\,\Delta T \qquad \text{Eq 8}$$

where, as before, Q is the airflow rate in the volume V, and $\bar{C}$ is the average tracer gas concentration measured by say, the GC.

Equation 8 allows the airflow rate, Q, in V to be estimated by GC/tracer gas techniques.

The percentage of tracer gas recovered, R_p, at the detector can be written as:

$$R_p = (V_D/V_s) \times 10^2 \qquad \text{Eq 9}$$

This quantity is related to δ by the simple relationship $R_p = 10^2\delta$.

The volume of tracer gas released by the source, i.e., V_s, can be estimated from the loss of mass of the bottle (container) over the release time ΔT as follows. From the ideal gas law:

$$V_s = n(RT/P) = n\,V_o \qquad \text{Eq 10}$$

where n is the number of moles of tracer gas released, and RT/P represents the normal volume V_o, of a perfect gas (at NTP, $V_o = 2.24136 \times 10^{-2}$ m^3/mole).

The number of moles of tracer gas released can be estimated from the expression below:

$$n = \Delta M/M_w \qquad \text{Eq 11}$$

where, ΔM is the loss of mass of the gas container, and M_w is the molecular weight of the tracer gas. For SF_6, $M_w = 146.054$, and Equation 10 becomes:

$$V_s = 15.346 \times 10^{-2} \Delta M \qquad \text{Eq 12}$$

where, V_s is in litres if ΔM is given in grams.

Alternatively, V_s can be estimated from the flow-rate at which the tracer gas mixture (i.e., tracer gas mixed with a carrier gas), q_B, the tracer gas concentration in the gas mixture container, C_B, and the release time, ΔT, as follows:

$$V_s = q_B C_B \Delta T \qquad \text{Eq 13}$$

Before proceeding to the principles of operation, operational procedures and practical applications of tracer gases and gas chromatography, a brief description of the terms used in ventilation work is given below. This is necessary because of the proliferation of terminology, and the freedom with which some terms are used in the literature which often confuse the reader.

DEFINITIONS

In reviewing the literature, the reader will be bewildered, and often confused, about the diverse terminology used in ventilation, and ventilation-related work. It is, for instance, not uncommon to find all of the following terms in the same paper:

1. residence time,
2. transit time,
3. clearance time,
4. age of air,
5. ventilation rate,
6. rate of air exchange,
7. rate of air renewal,
8. number of air exchanges per unit time,
9. air flow,

10. mass flow, and

11. flow rate.

Because different terms may mean different things to different people, and because the same terms may have different meanings to different people it is important to standardize the terminology used for the sake of simplicity, and in the interest of saving time.

Items 5, and 9 to 11, namely, ventilation rate, airflow, mass flow, and flow rate are commonly used interchangeably in the bibliography to indicate the rate of flow of air through a given experimental or 'test' volume V. Item 6 (rate of air exchange), and item 7 (rate of air renewal) have identical, although confusing meanings. Sometimes they are used as synonyms to item 8 (number of air exchanges per unit time). However, they may also be used to indicate air flow rate. In what follows, the terminology, air flow rate, or ventilation rate (item 5), will be used indistinguishably and equivalent to items 9 to 11. Items 6 and 7, on the other hand, will be used as identical to item 8.

The meaning of item 8 (number of air exchanges per unit time) should be clear enough; it simply indicates the number of complete air changes within a given volume V. Item 3 (clearance time) is the converse of item 8, namely, it can be defined as the time taken for a complete air change to occur within a given volume V. Transit time (item 2) can be defined as the time taken for a (hypothetical) differential layer of air to travel from point A to point B defining a volume V. If plug flow and perfect air mixing are assumed, the transit time and clearance time can be taken as synonymous.

The age of air is a rather ambiguous term. In its more general sense, it may mean the time spent by a given volume of air within a particular volume V. In this context, the age of air can be related to the transit time, or any other terminology indicated in items 1 to 3.

Residence time is another loosely used term. Often this term is used to indicate the time spent by ventilation air in a given volume V. From this standpoint, residence time is no different from age of air, transit time, and other terminology already discussed.

In the context of this paper, residence time (unless otherwise specified) will be used to indicate the time elapsed for 50% air renewal within the volume V. This is a useful variable in relation with tracer gas/GC work, and in agreement with its usage by numerous researchers.

PRINCIPLES OF OPERATION

In its simplest form or situation, e.g., a mine drift or mine shaft with no air leakages and no branching, splitting, or junctions (nodal points), the principle of field operation for determining the airflow characteristics by tracer gas analysis is fairly straightforward, namely, it consists of the following. Tracer gas is released at a given time t at one point A and samples of the gas are collected (continuously or intermittently) at a point B. (The region between points A and B defines the area of interest for which airflow data are sought.) The intensity (strength) of the sample, i.e., concentration of the tracer gas in the air sample collected, and the time elapsed between the release of the tracer gas at point A and the arrival of the diluted sample at point B provides the necessary information for determining important ventilation variables such as volumetric airflow rate and air residence time.

The release of tracer gas at point A is usually realized using a laboratory lecture bottle where the gas is kept under pressure. (If large quantities of tracer gas are to be used, larger gas containers than the conventional laboratory lecture bottles may be required.) The concentration and pressure of the tracer gas in the gas container are important variables

necessary in the calculation of ventilation parameters by tracer gas techniques.

Collection of tracer gas air samples at point B can be done using special syringes, vials, and air bags which can subsequently be analyzed by means of a laboratory-based gas chromatograph, or alternatively, in situ, by means of a field portable gas chromatograph located at point B. In the latter case, air samples are directly collected and analyzed by the gas chromatograph eliminating the need for time consuming air bags, and other means of air sampling, and the risk of loss of sample by leakage, and other problems.

There are two basically different techniques of tracer gas release which are of practical interest, namely:

1. continuous release, and
2. pulsed release.

In the first case, tracer gas from the pressurized container is continuously released at a constant flow rate for a given period until the sample concentration measured at point B attains a steady-state, i.e., constant, condition. At this point, the release of tracer gas at point A is terminated while gas samples are continuously taken at point B, usually at fixed time intervals, until the gas concentration decreases to either a background level, or to a sufficiently low level to permit proper analysis of the concentration versus time profile for calculation purposes. From the graphical characteristics of the gas concentration versus time 'decay' curve, air residence, air clearance time, and air flow can be determined. Continuous pulse release (injection) is illustrated in Figure 1.

In the second case, short pulses (bursts) of tracer gas from a pressurized container (or a series of syringes filled with a constant amount of gas) are released at regular intervals at point A, which are also detected, some time later at fixed time intervals at point B. As for the case of

continuous injection, the release of tracer gas at point A is interrupted when the gas sample concentration at point B reaches a constant value. The graphical profile of the concentration 'pulse train' versus time enables calculation of the ventilation variables of interest. Pulsed injection (release) is illustrated in Figure 2.

In simple field situations, one tracer gas and one gas chromatograph is all that is usually needed for a complete description of ventilation conditions. However, in more complex cases, e.g., leakage, recirculation, splitting, branching, close looping and the like, a somewhat more elaborate experimental strategy may be required. It should be noted that the main emphasis is placed in this report on experimental procedures which make direct use of a gas chromatograph in the field, i.e., direct in situ measurements as opposed to the case of field gas sample collection followed by subsequent analysis of the samples using a laboratory-based gas chromatograph.

In complex field ventilation conditions, experimental strategies other than the conventional one tracer gas/one field gas chromatograph are required unless extensive grab-sampling surveys are undertaken, followed by laboratory measurements. There are three basic strategies that can be implemented to study complex ventilation conditions, namely:

1. Use of a given tracer gas and several field gas chromatographs placed at different locations;
2. Use of several (different) tracer gases and one field gas chromatograph; and
3. Combination of items 1 and 2.

The advantages and disadvantages of item 1 and 2 depend on particular field conditions, availability of manpower, and other important considerations. The methodology suggested in item 3 is only justifiable under very complex field situations.

ADVANTAGES AND DISADVANTAGES OF PULSED (AND DECAY) INJECTION OVER CONTINUOUS INJECTION

In general, pulse tracer injection is preferred to continuous injection primarily because of the substantial savings in the amount of tracer gas used for experimentation. Analysis of the data in this case is, however, somewhat more complicated than for the case of continuous injection. Variables of importance in pulse injection are the duration of the pulse and, above all, the pulse frequency, i.e., the time elapsed between two successive releases of tracer gas.

If the pulse frequency is too high, the GC, or whatever other detection method or technique is in use, will not be able to resolve individual pulses because of the finite time taken by the detector to identify and process the signal. If, however, the pulse frequency is too low, i.e., pulses too widely spaced, valuable information may be lost. The pulse width, on the other hand, should be short but perfectly defined. An excessively long pulse or a relatively high pulse frequency may resemble a succession of decay (pulse) injections (see below) or, in the extreme case, a continuous injection.

Pulse injection has the added advantage that because it requires minimal addition of tracer gas to the volume V, the latter is soon cleared and ready for another test. Pulse and decay injection techniques can be effected by means of solenoid valves.

Continuous injection is conceptually simpler to understand and, in most cases, to analyze than decay injection or pulse injection. However, in addition to the large quantities of (expensive) tracer gas needed for experimentation, it has another drawback, namely, the difficulty of keeping a constant release of tracer gas mixture from the container into the volume V for extended periods. Tracer flow rate variation during release reflects in the detection of the tracer gas concentration by, say, the GC, and hence, the

overall accuracy of the analysis.

Decay (pulse) injection (Figure 3) represents an intermediate case between pulse injection and continuous injection and, as such, it exhibits in some instances advantages and disadvantages over the latter two injection methods. To the knowledge of the author, this injection modality is not in wide use.

PRACTICAL APPLICATIONS OF TRACER GAS TECHNIQUES IN UNDERGROUND URANIUM MINES AND MILLS

There are numerous potential practical applications of radioactive and non-radioactive tracer gas techniques to underground uranium mines and uranium mills. It is, of course, of great practical interest to compare non-radioactive tracer gas methods, e.g., SF_6/GC, with radioactive (man-made or naturally occurring) airborne radioactive tracer element methods. Although of general applicability, the material in this section is meant specifically for SF_6 and some fluorocarbons. Radioactive tracers are dealt with in the next three sections.

The practical application of gas chromatographic techniques includes the measurement of volumetric airflow rates, residence times (RT), and clearance times (CT). A reduced number of cases to which these techniques will be applied to shortly are listed below:

1. Measurement of air flow rate (Q), RT, and CT in a mine drift;
2. Measurement of air losses between two arbitrary points of a mine drift;
3. Measurement of RT and CT in a dead-end stope and drift heading where ventilation is effected by means of a secondary (auxiliary) fan and ventilation tubing;
4. Measurement of RT and CR in a 'flow-through' ventilated stope;
5. Determination of the existence, and quantification, of recirculation of

air in:

i) a series of dead-end stopes ventilated by secondary (auxiliary) fans;

ii) a main ventilation drift provided with a booster fan for ventilation purposes.

Items 1 to 5 will receive special consideration as part of the AECB contract with CANMET (EMR) during the 1989/90 FY. These experimental situations are depicted in Figures 4 to 6.

Because the primary objective of (forced) mechanical ventilation is to reduce airborne pollutants, it is of obvious interest to determine the efficiency of ventilation in reducing radon (thoron) and its decay products in underground (U/G) uranium mines and uranium mills. This requires careful, accurate, and extensive monitoring of these radioactive pollutants to be carried out parallel to ventilation studies. In order to do so, radon and radon progeny monitors should be placed at locations where 'conventional' tracer gas samples, e.g., SF_6, are taken, and also, because of the special physical nature of the above naturally occurring radioisotopes, at other locations as well.

Concurrent measurements of conventional tracer gas samples and naturally-occurring radioisotopes such as ^{222}Rn and its progeny (and also ^{220}Rn and progeny) in U/G uranium mines are of particular interest in recirculation studies to assess the usefulness and limits of application of this ventilation modality in reducing naturally-occurring radioactivity levels. Concurrent measurements of ^{222}Rn, ^{220}Rn and their decay products, and ventilation variables such as Q, RT and CT are also of great practical and theoretical interest to verify the validity and applicability limits of theoretical (radiation) mine models. These and other topics, such as the use of naturally-occurring and man-made radioactive elements for tracer studies, will be dealt with in detail in a separate report.

The above discussion brings us to the heart of the experimental procedure, namely, the field work strategy. Because of the complexity of the topic, it is natural to expect a complex strategy to conduct the field work. This will be outlined in detail in a forthcoming report. However, the following can be anticipated at this stage, namely, monitoring procedures will consist of both continuous and discrete, i.e., grab-sampling. Furthermore, sample processing will be conducted both in situ and in the laboratory. In addition, samples will be taken throughout the experimental work at fixed locations. Finally, radioactivity samples and tracer gas samples (e.g., SF_6) will be taken concurrently in most cases.

The conventional methodologies (experimental and analytical procedures) used to determine items 1 to 5 by chemical tracer gases, such as SF_6, are briefly examined below.

1. MEASUREMENT OF THE VOLUMETRIC AIRFLOW RATE, Q

The volumetric air flow rate, Q, in say, an airway, air drift, or elevator shaft can be determined by means of Equation 8 (see section entitled 'Theoretical Background'). If no air losses (leakage) occur between point A (SF_6 gas release) and point B (sampling station), then $R_p = 100\%$, i.e., $\delta = 1$, and $V_D = V_s$, where V_s is given by equations 12 and 13.

Once Q is known, the volume V of the mine section of interest can be calculated if the clearance time (CT) is known. Assuming perfect mixing and plug-flow, the following expression applies: $V = Q(CT)$. The clearance time and residence time (RT) can be determined experimentally as indicated in item 2. Conversely, if V is known, CT can be estimated using the above expression.

2. DETERMINATION OF AIR RESIDENCE TIME AND AIR CLEARANCE TIME

The residence time (RT) and clearance time (CT) can be determined from their definitions in the text and the tracer gas concentration versus time profile (see Figure 7), as follows. From the decay portion of the tracer gas

concentration versus time profile, the CT is given as the time taken by the tracer gas concentration to decrease from its constant, steady-state, value to a negligible fraction of this value, i.e., to background levels. The time elapsed for 50% reduction of the steady-state tracer gas concentration value to take place gives the residence time according to our previous definition. Similar arguments apply equally well to the build-up portion of the tracer gas concentration versus time profile. Namely, the time taken for the tracer gas concentration to attain 50% and 100% of its final, i.e., steady-state, value gives the residence time and clearance time, respectively. It should be noted that the build-up (rise) and decay portions of the tracer gas concentration versus time profile arise from the sudden release and interruption of the tracer gas, respectively. It is also worthwhile noting that the rise and decay portions of the profile may not be strictly symmetrical because of transient effects during the initial mixing process of tracer gas and air.

3. DETERMINATION OF AIR LEAKAGE BETWEEN TWO POINTS OF A VENTILATION CIRCUIT

There are two possible cases, namely, air loss between the two points of the circuit, or air leaking into the circuit. Assuming good mixing and no complicating factors such as recirculation, the following apply to the loss of air between point A (release of tracer gas) and point B (collection of sample):

$$V_D \neq V_s, \text{ and } V_D < V_s$$

Hence, $\delta < 1$ or $R_P < 100\%$. The ratio V_D/V_s (=δ) provides a measure of the air loss in the ventilation circuit. It is clear that if $\delta = 1$ ($R_P = 100\%$), i.e., $V_D = V_s$, there is no loss of air in the circuit. Likewise, if $\delta = 0$ ($R_P = 0\%$), i.e., $V_D = 0$, all the air is leaking out the circuit, and hence, no air reaches point B. The above arguments follow from the fact that if there is proper mixing of the tracer gas and ventilation air, then a loss of air must also cause a corresponding loss of tracer gas.

If air leaks into the ventilation circuit, the amount of tracer gas is still preserved although its concentration in air will be correspondingly reduced because of the influx of air. It is possible to detect positive leakage (i.e., air leaking in) in a ventilation circuit because in most cases if the leakage is large enough it may cause undesirable effects such as eddy currents, deficient mixing and/or partial recirculation. In all these cases, a substantial distortion of the tracer gas concentration versus time profile may result. Depending on the details of this distortion, e.g., irregularities, concentration uneveness, and/or multiple peaks appearing in the profile, it is possible to draw some conclusions regarding potential positive leakage into the ventilation circuit.

4. DETERMINATION OF THE EXISTENCE, AND QUANTIFICATION, OF RECIRCULATION OF AIR

Air can be recirculated in a ventilation circuit in a controlled fashion for specific purposes such as a means of energy conservation. Quite often, however, recirculation of air in a ventilation circuit is accidental and caused, say, by air leakages in the circuit.

Because in most cases encountered in actual practice, air recirculation patterns in ventilation circuits are varied and, hence, can be quite complex, quantification of recirculation is not an easy task. This situation is often complicated by incomplete air mixing, eddy currents, local air velocity changes, multiple air passes, local air leakage, and other influences.

In its simplest form, a recirculation circuit can be represented as shown in Figure 8. Hence, if tracer gas is released at point A, the tracer gas/ventilation air mixture will follow two distinct paths, namely, the direct path AKXYZB (no recirculation) and the longer path of recirculation, i.e., AKXYZKXYZB. Because the lengths of these two paths are different, two tracer gas 'pulses' will be detected at point B: one from the direct path at time, say, t_0, and the other from the recirculation path, some time later, say, t_1.

The above holds true for 'single pass' situations. If multiple air passes occur the situation can become very complicated and multiple peaks, clean or distorted, are most likely to appear.

Assuming none of the disturbing and complicating effects noted above are applicable, the tracer gas concentration versus time trace (profile), for the simplest recirculation network (see Figure 9), should show two distinct concentration maxima appearing with a time lag relative to one another. From the shapes of the traces, the maximum concentrations, the time difference between the two maxima, the concentration versus time integrals under the tracers, and the ratio of these integrals, it is possible to determine the existence of recirculated air, the residence and clearance times, and also some geometrical data regarding the experimental site.

A few air recirculation situations of practical interest, frequently encountered in ventilation circuits, are depicted in Figures 4 (lower graph) and 5,6. These situations will be investigated experimentally shortly, and the results will be reported separately in a forthcoming report.

It should be noted that the success and reliability of some of the measurements discussed above depend a great deal on the capabilities of the instrumentation, the technique used, and a number of other factors including the geometrical characteristics of the experimental site, ventilation variables such as air velocity, and other practical considerations. For instance, the instrument should be capable of detecting the tracer gas and should process the signal produced in the detector with sufficient speed so that closely spaced (in time) tracer gas samples arriving at the instrument can be detected and resolved with adequate accuracy and resolution.

Finally, the reader should be aware that a great deal of additional information can be obtained from tracer gas concentration versus time profiles, obtained by either continuous injection or pulse injection

techniques, by resorting to some simple mathematical manipulation of the data. Two such examples are the differentiation of a continuous trace, and the integration of a pulse train. These two graphico-mathematical operations are, actually, the converse of one another. Both operations involve digitization of the data followed by a mathematical operation, i.e., either differentiation or integration. This technique enables the conversion of a continuous trace into an equivalent pulse injection, and vice versa, which results in a wealth of additional data for analysis.

RADIOACTIVE TRACERS

Radioactive tracer techniques do not differ fundamentally from the techniques used for non-radioactive (chemical) tracers such as SF_6, CO_2, CH_4, C_3H_8, and other chemical tracers, except for the detection system and the associated data processing instrumentation. A distinct complicating factor is, however, worth mentioning, namely, radioactive tracers are not stable, i.e., their concentration in air decreases with time with a characteristic half-life according to well understood laws. For this reason, the choice of radionuclide is of paramount importance in certain applications where it is desirable for the half-life of the radioactive tracer to be much longer than the duration of the experiment. If this condition is satisfied the experimental procedure and the analysis of the data are greatly simplified.

The above half-life requirement severely limits the choice of airborne man-made radioactive tracers to ^{85}Kr, ^{133}Xe and ^{79}Kr. The half-life of ^{41}Ar (1.827 h), another gaseous radioactive tracer, is too short to be of practical use, except in very special cases. The case for naturally-occurring radioactive tracers of interest in U/G uranium mines (and in reality in all U/G mines, in general), e.g., ^{222}Rn, ^{220}Rn, and their respective decay products, is somewhat different than that for man-made radioactive tracers.

Because of this, these two groups of radioactive tracers will be dealt with separately.

Because quantification of radioactive tracers is, in general, faster (i.e., better time resolution) than for chemical tracers such as SF_6 using GC techniques, the use of radioactive tracers offers certain special advantages over chemical tracers. Another distinct advantage of radioactive tracers is the simplicity of the instrumentation used, e.g., GM tubes in most cases, combined with the availability and low cost of this instrumentation.

Time resolution and detection sensitivity are two important variables that partly depend on the type of radiation to be measured (α, β or γ), and the kind of detector used. Hence, the kind of radiation (used for tracing purposes) emitted by the radionuclide is important because it determines the specific use of the tracer. For instance, penetrating radiation such as γ-rays enable 'tracking' of radionuclides externally from, say, metal ventilation ducting which is not possible when using α- and/or β-emitters. Table 2 shows a number of radioactive tracers of interest, their half-lives, modes of decay, method of production and other data of interest.

APPLICATIONS OF RADIOACTIVE TRACERS

Gaseous man-made radioactive tracers have been used for over two decades. Their uses include:

1. Ventilation measurements such as determinations of air exchange rates;
2. Measurement of dilution factors;
3. Establishment of airflow patterns in complex geometrical configurations; and
4. Dispersion studies.

Naturally occurring radionuclides formed in the atmosphere and radionuclides formed in atom bomb detonations have been used in the

investigation of large scale processes in the atmosphere.

Pollution studies have been carried out by measuring the atmospheric distribution of ^{222}Rn and ^{220}Rn, and their decay products, in coastal urban areas to determine the mixing rates between street air and the atmosphere above a city. A review of the work done with radioactive tracers until 1977, on which the present discussion is based, has been given by Gilath (4) elsewhere.

The use of ^{222}Rn, ^{220}Rn and their decay products as indicators of ventilation conditions in U/G uranium and non-uranium mines has been suggested, and applied, by Bigu (1-3).

Other interesting types of tracers are the hybrid tracers, also known as activable tracers. These tracers have been suggested for pollution and dispersion studies, and are conventional aerosols loaded with activated elements (by, say, neutron activation techniques) or man-made radionuclides 'tagged' to the aerosol carrier (cited in ref. 4). Air samples for tracer analysis are usually taken using a sampling filter/high volume sampling pump arrangement, or by using cascade impactors for aerosol size characterization.

Before proceeding to discuss the experimental procedures, and theoretical background, pertinent to using radioactive tracers, a brief summary of the advantages and disadvantages of radioactive and chemical tracers will be given below.

Man-made airborne radioactive tracers offer a number of advantages over some chemical tracers, notably SF_6 and fluorocarbons, namely:

1. It requires inexpensive instrumentation such as GM tubes;
2. Data analysis is fairly simple;
3. Radioactive tracers are easy to detect on a continuous basis because of the time resolution of the detector and its associated electronic circuitry;

4. Because of the high penetration power of some of the radiation emitted by radioactive tracers, particularly γ-rays, they can be used in ventilation ducting with external monitoring of the radiation; and
5. In some cases, no special production procedures or techniques are necessary because they are found as by-products of U fission (fission products) in the core of nuclear reactors, e.g., ^{85}Kr and ^{133}Xe.

However, radioactive tracers have some disadvantages also:

1. Except for a few cases, e.g., ^{85}Kr (radioactive half-life: 10.8 y), radioactive tracers have a limited shelf life because of radioactive decay.
2. Production of some radioactive tracers such as ^{41}Ar may be expensive because they are produced by neutron irradiation of certain elements, e.g., $^{40}Ar\ (n,\gamma)\ ^{41}Ar$ or $^{41}K(n,p)\ ^{41}Ar$. Because of the low yields, high neutron fluxes are required which limits the above nuclear procedure to nuclear reactors.
3. Although at the concentrations they are used for ventilation studies the utilization of radioactive tracers causes no appreciable biological hazard, public perception is negative toward the use of radioactive materials, and their use is, therefore, limited to specific cases.

Although some man-made radioactive tracers, such as ^{85}Kr, were used before some chemical tracers, e.g. SF_6, the latter is increasingly being favoured.

Naturally-occurring radioactive tracers such as ^{222}Rn and its progeny (and ^{220}Rn and its progeny) are the cheapest and, to some extent, the easiest to deal with if advantage is taken to use these tracers in their natural environment as suggested elsewhere (1-3).

Some specific practical applications, and theoretical background information, to ventilation studies are discussed below.

RADIOACTIVE TRACERS IN VENTILATION STUDIES

Before discussing specific applications of radioactive tracers, some theoretical background on the analytical methodology used is in order.

A. THEORETICAL BACKGROUND

Two methods are extensively used in ventilation studies using radioactive tracers, namely, the pulse-velocity method (7), and the total-count method (8), both cited in ref. 5.

a) Pulse-Velocity Method

In the pulse velocity method a short 'pulse' of radioactive tracer is released at a given point in, say, a regularly shaped air duct. If an air-mixing mode developed by Exall (12) is used, it can be shown (5) that the air concentration of radioactive tracer at time t and distance z from the injection point, i.e., C(z,t) is given by:

$$C(z,t) = (Co/(4D\pi t))\ \exp(-(z-vt)^2/4Dt) \qquad \text{Eq 14}$$

where, Co is the initial (input) concentration of radioactive tracer;

D is the diffusion coefficient of the tracer in air;

t is the time elapsed from t=0;

v is the velocity of air in the duct.

The experimentally determined values of the recorded radioactive pulse trace of count rate versus time, i.e., at a known distance z, C(z,t) can be fitted by a least-squares computer program to the above equation by varying the values of v and D. The value of v that best fits the equation gives the speed of the air in the duct.

This method does not require calibration of the instrumentation or the radioactive source. However, the method can only be used in situations where the air duct has a uniform cross-section. The use of the pulse-velocity method would, therefore, be rather limited in the case of mine shafts, drifts,

stopes, and the like, if their cross-sections depart significantly from uniformity. (Note: it is assumed that the pulse velocity method can be extended, physically and geometrically speaking to apply to scaled-up models.)

It is clear that the air velocity in regularly-shaped structures can be obtained by timing the passage of a radioactive tracer pulse between two detectors, or alternatively, between the time of release of the tracer pulse and the time taken by the pulse to pass a detector situated a known distance (z) downstream from the point of release.

b) Total-Count Method

In this method a known amount of radioactive tracer is added to the flow of air, and the radioactivity at a given point downstream is measured by time-integrating techniques (4,8). Calling:

Q the air flow rate through a cross-section S corresponding to a volume of the mine V,

A the total activity of the radioactive tracer injected into V; and

N(t) the net count rate measured by the detector at time t at a distance, z, downstream from the release of the radioactive tracer.

We can write a simple relationship between the above variables. Taking into account that the total (integrated) count recorded by the detector during the passage of the radioactive tracer pulse, namely, N is given by:

$$N = \int_0^\infty N(t)\, dt$$

and that N is directly proportional to A and inversely proportional to the velocity, v, of the pulse or air, where $v = Q/S$, we can write:

$$N = k(A/Q)$$

or, alternatively,

$$A = KNQ \qquad \text{Eq 15}$$

where $K = 1/k$ is a proportionality factor which depends on the detector counting efficiency, its sensitivity, and, if a β-emitting tracer is used, on

the density of air.

From the above equation it is not difficult to see that the total-count method requires an accurate value for the activity of the radioactive tracer and the proportionality constant K, which implies calibration of the detector. However, cross-sectional area, S, constancy, unlike with the pulse-velocity method, is not necessary.

A variant of the total-count method has been suggested, and used, namely a continuous injection instead of a pulse (4). These methods, are, in principle, identical to the methods used for chemical tracers discussed previously.

B. VENTILATION STUDIES USING AIRBORNE MAN-MADE RADIOACTIVE TRACERS

The two following applications have been discussed by Gilath (4) and although ^{85}Kr has been suggested as the radioactive tracer, the experimental procedure is general in its approach and can be extended to any radioactive tracer, provided its radioactive half-life is compatible with the nature of the experiment or measurement.

One application of direct practical interest is that of determining the air flowrate, Q, in a given enclosure of volume V. In this case, the radioactive tracer is introduced into V, mixed homogeneously with the air and the tracer concentration in V is carefully measured. The air flow rate can be found from the decrease in radioactive tracer concentration versus time, C(t). This concentration decrease is exponential and has the same analytical form as that derived for chemical tracers (see equation 3), i.e.,

$$C(t) = C_o\, e^{-(Q/V)t} \qquad \text{Eq 16}$$

This method also enables mixing conditions to be determined by measuring C(t) at different locations in V simultaneously. Under good mixing conditions, C(t) should be uniform over the volume V.

Another practical application of radioactive tracers is in the

determination of ventilation dilution factors, F. The dilution factor is defined by the following expression:

$$F = q/(q + Q) \qquad \text{Eq 17}$$

where q is the flow rate of, say, a polluting agent in the air. If the polluting agent is discharged in V at a flowrate q and concentration C_o, the ultimate or steady-state concentration of the pollutant in V will be C, and by the mass conservation law, namely:

$$qC_o = (q + Q)C \ , \qquad \text{Eq 18}$$

Equation 17 can be derived, and another definition of the dilution factor can also be expressed as $F = C/C_o$.

The dilution factor, F, can be determined using the total count method discussed above as follows. A short pulse of radioactive tracer of activity A is injected into the stream of the polluting agent discharged into V at a flow rate q. If a and a_o are defined as the steady-state specific activity in V and the specific activity at the source, respectively, the dilution factor can now be written as:

$$F = a/a_o \qquad \text{Eq 19}$$

it can be shown (4) that:

$$F = qN/\epsilon A \qquad \text{Eq 20}$$

where N has the usual meaning (see above), and ϵ is the detection sensitivity, say cpm/Bq m^{-3}. Alternatively, if F is known, pollutant discharge flow rate, q, can be calculated using equation 20.

The same methods and principles discussed above are, of course, equally applicable to chemical tracers. Although use is quite often made of either chemical tracers or radioactive tracers, there is a distinct advantage, in some cases, in using both methods (i.e., tracer kinds) concurrently in order to either compare experimental data or to conduct complementary studies. The latter is important because each method offers advantages over the other, and

also because some kind of data may be more readily available by one method than by another.

FINAL REMARKS

It is not possible to deal here with all aspects of tracer gases and their practical applications. The reader should consult the published literature on the field for further information. A sample of the publications in the area of interest here is given in references 13 to 51.

Finally, a technical description of the gas chromatograph which will be used for the field work is given in the form of an Appendix.

REFERENCES

1. Bigu, J., "Theoretical models for determining ^{222}Rn and ^{220}Rn progeny levels in Canadian underground U-mines - a comparison with experimental data"; Health Physics, vol. 48, pp. 371-399, 1985.

2. Bigu, J., Schryer, D., "Radioactivity emissions from bacterially-assisted leaching of uranium stopes"; Division Report MRL 87-174(TR), CANMET, Energy, Mines and Resources Canada; 1987.

3. Bigu, J., "Radioactive and non-radioactive (tracer) gas techniques for studying ventilation conditions in working environments"; to be presented to 4th U.S. Mine Ventilation Symp., University of California, Berkeley, U.S.A., June 5-7, 1989.

4. Gilath, C., "Ventilation and air pollution studies using radioactive tracers. A critical review"; Int J Appl Radiation and Radioisotopes, vol. 28, pp. 847-854, 1977.

5. Snyman, G.C., Short, R.C. and Basson, J.K., "Airflow measurement of the ventilation system of Kinross Gold Mine, using radioactive Krypton-85"; Proc 3rd Int Mine Ventilation Congress, Harrogate, U.K., 1984.

6. Margrita, R. and Santos-Cottin, H., "A new tracer gas technique in industrial applications: Krypton-79": Appl Radiat Isot, vol. 39, No. 4, p. 357, 1988. (Int. J. Radiat. Appl. Instrum. Part A.)

7. Clayton, C.G., "The measurement of flow of liquids and gases using radioactive isotopes"; The British Nuclear Energy Society, vol. 3, No. 4, pp. 252-268, 1964.

8. Hull, D.E., "The total-count technique: a new principle in flow measurement"; Int J Appl Radiat and Isot, vol. 4, pp. 1-15, 1958.

9. Abbott, D. and Andrews, R.S., "An Introduction to Chromatography", Houghton Mifflin Co., Boston, 1965.

10. Bobbitt, J.M., Schwarting, A.E. and Gritter, R.J., "Introduction to Chromatography", D. Van Nostrans Co., New York, 1968.

11. Drivas, P.J., Simmonds, P.G. and Shair, F.H., "Experimental characterization of ventilation systems in buildings"; Environ Sci Tech, vol. 6, No. 7, pp. 609-614, 1972.

12. Exall, D.I., "A study of the use of statistical turbulence parameters in correlating axial dispersion data in the central core of air flowing in a pipe; Ph.D. Thesis, Dept. of Chemical Engineering, University of Natal, 1970.

13. Jordan, D.W., "A theoretical study of the diffusion of tracer gas in an airway", Quart J Mech & Appl Math, vol. 14, Pt. 2, pp. 203-222, 1961.

14. Hampl, V., Niemela, R., Shulman, S. and Bartley, D.L., "Use of tracer gas technique for industrial exhaust hood efficiency evaluation - where to sample?"; Am Ind Hyg Assoc J, vol. 47, No. 5, pp. 281-287, 1986.

15. Wann, J.M.R., Milner, A. and Wynne, A., "Some practical experiences using sulfur hexafluoride as a tracer gas to determine leakage rates in mine ventilation systems, mainly in the South Nottinghamshire area"; Mining Engineer, vol. 136, No. 191, pp. 391-404, 1977.

16. Hopton, F.J. and Rix, M.R.E., "Tracer gas review and tracer gas ventilation study of a tunnel boring machine": Ontario Research Foundation Reports P-4331/G-1 and P-4331/G-2, Sept/Dec. 1983.

17. James F. MacLaren Ltd., "SF_6 ventilation study at Agnew Lake mines, Ontario": CANMET, Energy, Mines and Resources Canada, Contract 23440-7-9106; (Report to EMR, Elliot Lake), March 1979.

18. Timko, R.J. and Thimons, E.D., "Sulfur hexafluoride as a mine ventilation research tool - recent field applications": U.S. Dept. of Mines, Bureau of Mines Report of Investigation RI-8735, 1982.

19. Thimons, E.D., Bielicki, R.J. and Kissell, F.N., "Using sulfur hexafluoride as a gaseous tracer to study ventilation systems in mines": U.S. Dept. of the Interior, Bureau of Mines Report of Investigation RI-7916, 1976.

20. Matta, J.E., Thimons, E.D. and Kissell, F.N., "Jet fan effectiveness as measured with SF_6 tracer gas": U.S. Dept. of the Interior, Bureau of Mines Report of Investigation RI-8310, 1978.

21. Thimons, E.D. and Kissell, F.N., "Tracer gas as an aid in mine ventilation analysis": U.S. Dept. of the Interior, Bureau of Mines Report of Investigation RI-7917, 1974.

22. Higgins, J., Sheila, E.H. and Shuttleworth, M.A., "A tracer gas technique for the measurement of airflow in headings"; Colliery Engineering, pp. 483-487, Nov. 1958.

23. Dietz, R.N. and Cote, E.A., "Tracing atmospheric pollutants by gas chromatographic determination of sulfur hexafluoride"; Envir. Sci. & Tech, vol. 7, No. 4, pp. 338-342, 1973.

24. Elias, L., McCooeye, M. and Gardner, G., "On-site measurement of atmospheric tracer gases": Geophys. Res. Letters, vol. 3, No. 1, pp. 17-20, 1976.

25. Wanninkhof, R., Ledwell, J.R. and Broecker, W.S., "Gas exchange-wind speed relation measured with sulfur hexafluoride on a lake"; Science, vol. 227, pp. 1224-1226, 1985.

26. Wippern, D. et al., "Characterization of fluidized bed reactors with gas tracer measurements"; Chem Eng Commun, vol. 10, pp. 307-330, 1981.

27. Sinden, F.W., "Multi-chamber theory of air infiltration"; Building & Environment, vol. 13, pp. 21-28, 1978.

28. Sandberg, M., "What is ventilation efficiency?"; Building Environment, vol. 16, pp. 123-135, 1981.

29. Kalliokoski, P., Niemelä, R. and Salmivaara, J., "The tracer gas technique - a useful tool for industrial hygiene"; Scand J Environ Health, vol. 6, pp. 123-130, 1980.

30. Grimsrud, D. et al., "An intercomparison of tracer gases used for air infiltration measurements"; ASHRAE Trans, vol. 86, No. 1, pp. 258-267, 1980.

31. Sandberg, M. and Svensson, A., "Measurements of ventilation efficiency by using the tracer gas technique"; Building Services Engineering Res & Tech, vol. 2, No. 3, pp. 119-126, 1981.

32. Danner, R.P., Nicoletti, M.P. and Al-Ameeri, R.S., "Determination of gas mixture adsorption equilibria by the tracer-pulse technique"; Chem. Engrg Sci, vol. 35, pp. 2129-2133, 1980.

33. Fediw, T.J., Nemeth, E.J. and Caram, H.S., "Tracer study to measure deposits and dispersion coefficients in large-diameter gas lines"; Chem Engrg Sci, vol. 36, pp. 1575-1577, 1981.

34. Heggen, R. and Oehme, M., "Columns for simultaneous gas chromatographic determination of ppt levels of the atmospheric tracers sulfur hexafluoride and bromotrifluoromethane in ambient air samples"; J of Chromatography, vol. 243, pp. 168-172, 1982.

35. Vinson, R.P., Volkwein, J.C. and Thimons, E.D., "SF_6 tracer gas tests of bagging-machine hood enclosures": U.S. Dept. of the Interior, Bureau of Mines Report of Investigation RI-8527, 1981.

36. Matta, J.E., Maksimovic, S.D. and Kissell, F.N., "Tracer gas method for measuring leakage through mine stoppings"; U.S. Dept. of the Interior, Bureau of Mines Report of Investigation RI-8324, 1978.

37. Vinson, R.P. and Kissell, F.N., "Three coal mine ventilation studies using sulfur hexafluoride tracer gas": U.S. Dept. of the Interior, Bureau of Mines Report of Investigation RI-8142, 1976.

38. Hampl, V. and Shulman, S., "Use of tracer gas techniques for industrial exhaust hood efficiency evaluation - application of sulfur hexafluoride for hood controlling particulate emissions": Am Ind Hyg Assoc J, vol. 46, No. 7, pp. 379-386, 1985.

39. Maugh II, T.H., "A new dimension in gas chromatography": Science, vol. 227, pp. 1570-1571, 1985.

40. Turk, A., Edmonds, S.M. and Mark, H.L., "Sulfur hexafluoride as a gas-air tracer": Envir Sci & Tech, vol. 2, No. 1, pp. 44-48, 1968.

41. Lamb, B.K., Vitols, V. and Skogvold, O., "Atmospheric tracer techniques and gas transport in the primary aluminum industry": J Air Pollution Control Assoc, vol. 30, No. 5, pp. 558-566, 1980.

42. Gilath, Ch., "Determination of the dilution of a gas discharged into a ventilated atmosphere": Int J Appl Radiat & Isotopes, vol. 22, pp. 671-675, 1971.

43. Nickola, P.W., Ludwick, J.D. and Ramsdell, J.V., "Atmospheric tracer technique employing ^{85}Kr and use of this technique in defining puff dimensions and transport speed"; Isotopes & Radiat Tech, vol. 9, No. 1, pp. 65-71, 1971.

44. Gerrard, M., "Measurement of ventilation rates with radioactive tracers": Isotopes & Radiat Tech, vol. 5, No. 4, pp. 278-280, 1968.

45. Hodkinson, J.R. and Leach, S.J., "The longitudinal dispersion of pulses of respirable dust and gas in ventilated mine workings, studied by a radioactive tracer technique"; Trans Inst Min Engrgs, vol 117, pp. 684-702, 1957-58.

46. Bakke, P., Leach, S.J. and Slack, A., "Some theoretical and experimental observations on the recirculation of mine ventilation"; Colliery Engineering, pp. 471-477, 1964.

47. Göthe, C.J., Bjurström, R., and Anker, K., "A simple method of estimating air recirculation in ventilation systems"; Am Ind Hyg Assoc J, vol. 49, No. 2, pp. 66-69, 1988.

48. Allan, J.A., "A review of controlled recirculation ventilation systems in U.K. collieries"; CIM Bull, vol. 76, No. 849, pp. 83-87, 1983.

49. Leach, S.J., "Ventilation of advance headings"; Colliery Engineering, pp. 510-516, 1966.

50. Jones, I.O., "The benefits of recirculation in mines"; Mine & Quarry Mech, pp. 133-139, 1983.

51. Leach, S.J. and Slack, A., "Recirculation of mine ventilation systems"; The Mining Engr, vol. 128, pp. 227-234, 1969.

Table 1 - Some characteristics of SF_6

Molecular weight	146.054
One mole of SF_6	0.146 054 kg
Sublimation point @ 101.325 kPa (1 atm)	209.45 K (-82.66°F)
Melting point @ 223.93 kPa (2.21 atm)	222.35 K (-59.44°F)
Critical temperature	318.69 K (113.97°F)
Critical pressure	3 759.158 kPa (37.1 atm)
Critical volume	1.356 dm^3/kg (198 cm^3/mol)
Critical density	0.736 kg/dm^3
Critical compressibility factor	0.267
Latent heat of fusion	
@ 222.35 K, 223.93 kPa (2.21 atm)	5.020 8 J/mol (1 200 cal/mol)
Heat of sublimation	
@ 209.45 K	23.598 kJ/mol (5 640 cal/mol)
Index of refraction, gas @ 101.325 kPa (1 atm), n_D	
@ 273.15 K	1.000 783
Dipole moment, gas	0 C.m
Dielectric constant, Gas	
@ 101.325 kPa and 298.15 K	1.002 049
Velocity of sound in SF_6 @ 303.15 K	138.4 m/s

DESCRIPTION

At room temperature and atmospheric pressure, sulphur hexafluoride is a colourless, odourless, nontoxic gas. It is readily liquified and is shipped in steel cylinders as a liquified gas under its own vapour pressure of 2 307.68 kPa [334.7 lbf/in^2 absolute (psia); 22.8 atm] at 294.26 K (70°F).

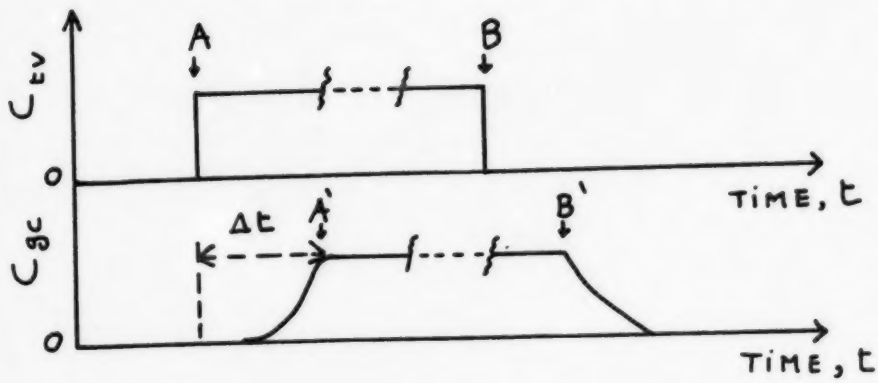
Sulphur hexafluoride is an octahedral molecule, with O_h point group symmetry and a symmetry number of twenty-four. The structural parameters are as follows: S-F bond length: 1.564 Å (1.564×10^{-10} m); F-S-F bond angle: 90°.

Sulphur hexafluoride has six normal modes of vibration, of which ν_1, ν_2, and ν_5 are Raman active, whereas only ν_3 and ν_4 are infrared active. The fundamental vibrational frequencies (in cm^{-1}) and mode assignments (in parentheses) are as follows: 770 (ν_1); 640 (ν_2); 522 (ν_3); 345 (ν_4); 615 (ν_5); 947 (ν_6).

Table 2 - Data for some potentially useful radioactive tracers

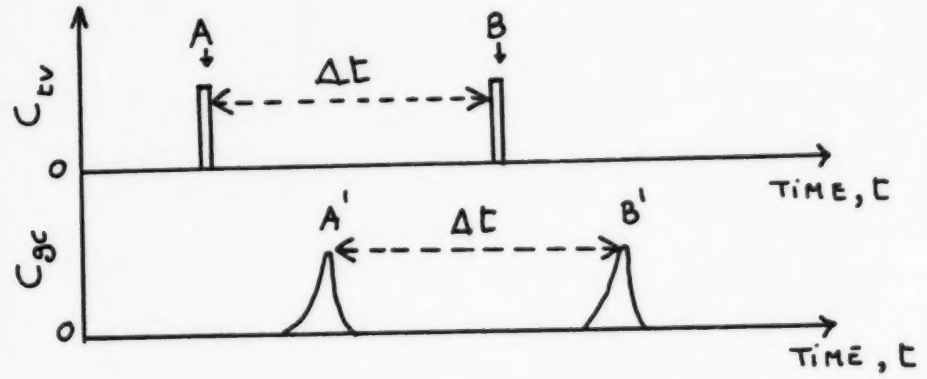
Radioisotope	Half-Life	Decay Mode	Production Method
^{85}Kr	10.4 y	β^-, γ	U(n,f)
^{41}Ar	1.85 h	β^-, γ	a) $^{40}Ar(n,\gamma)^{41}Ar$ b) $^{41}K(n,p)^{41}Ar$
^{133}Xe	5.65 d	β^-, γ	a) U(n,f) b) $^{132}Xe(n,\gamma)^{133}Xe$
^{79}Kr	34 h	K,β^+,γ	a) $^{79}Br(p,n)^{79}Kr$ b) $^{79}Br(d,2n)^{79}Kr$ c) $^{78}Kr(n,\gamma)^{79}Kr$

Notes:
1. The symbols β^- and β^+ are used to denote β-particle and positron decay, respectively.
2. K stands for K-electron capture.
3. The symbols n, f, d, and p stand for neutron, fission, deuteron and proton, respectively.



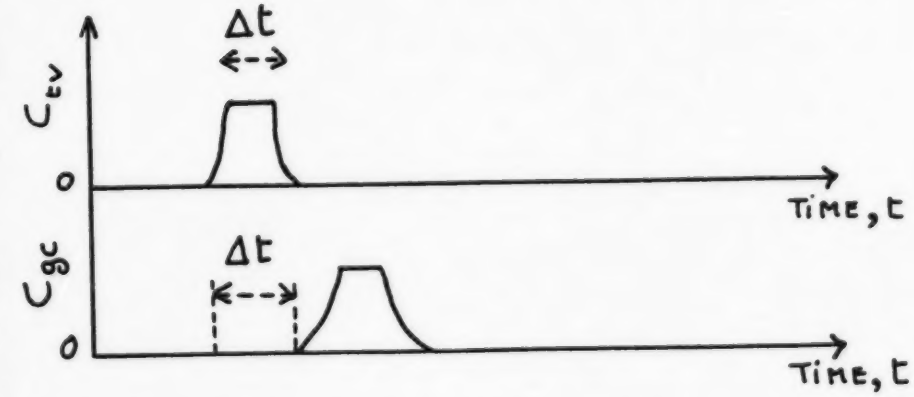
CONTINUOUS INJECTION

FIG. 1



PULSE INJECTION

FIG. 2



DECAY PULSE INJECTION

FIG. 3

Fig. 1 to 3 - Illustrations of continuous (Fig. 1), pulse (Fig. 2), and decay pulse (Fig. 3) injection. Upper and lower graphs of each figure represent tracer gas injection and detector response, respectively. The symbols C_{gc} and C_{tv} stand, respectively, for the tracer gas concentration measured with the gas chromatograph, and the tracer gas concentration in the 'test volume'.

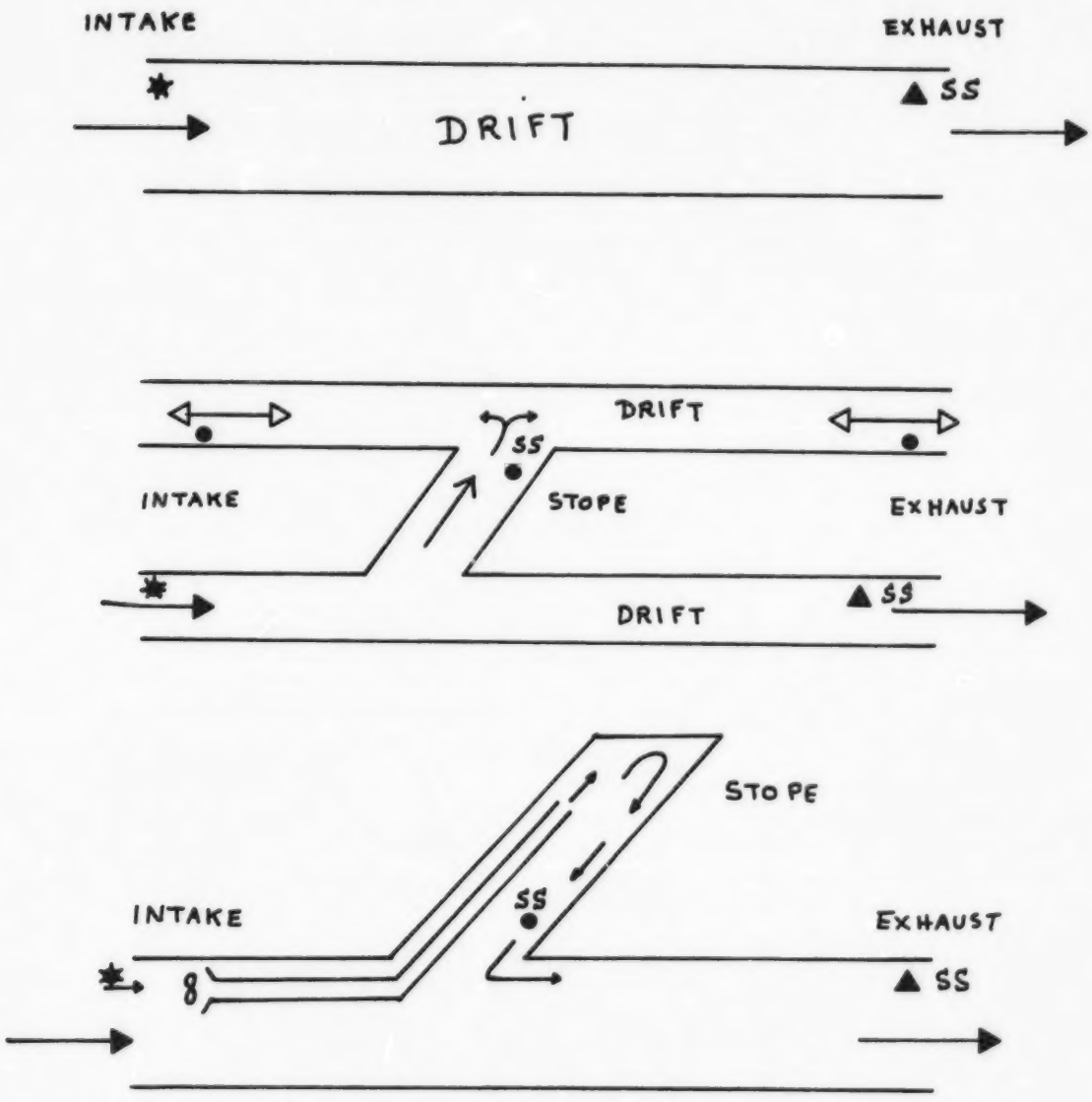


Fig. 4 - Experimental layout of some simple ventilation situations. The asterisk indicates tracer gas injection points. The solid circles and triangles indicate potentially useful sampling stations (SS).

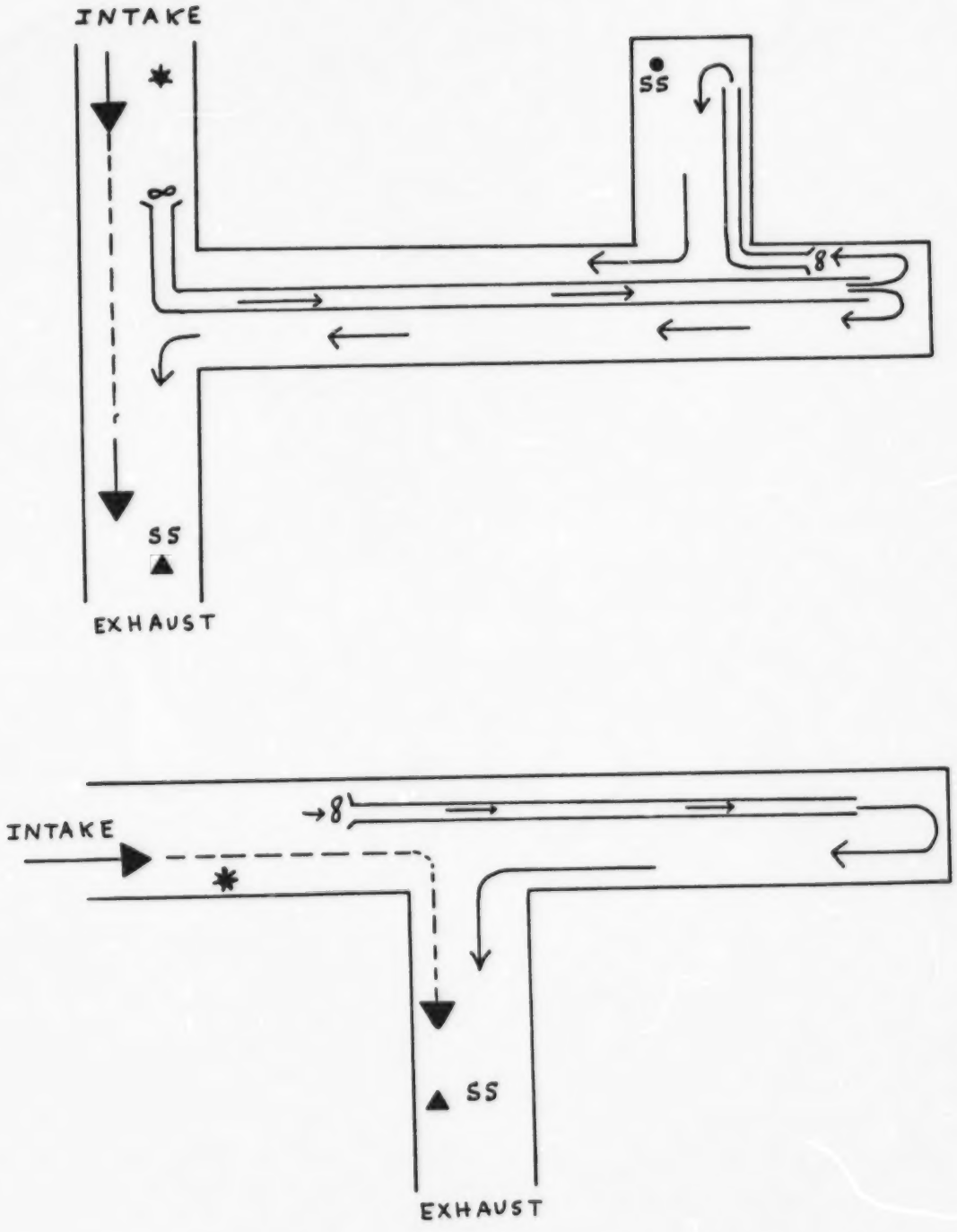


Fig. 5 - Experimental layout of some simple ventilation situations with recirculation. The asterisks are used to indicate tracer gas injection points. The solid circles and triangles indicate potentially useful sampling stations (SS).

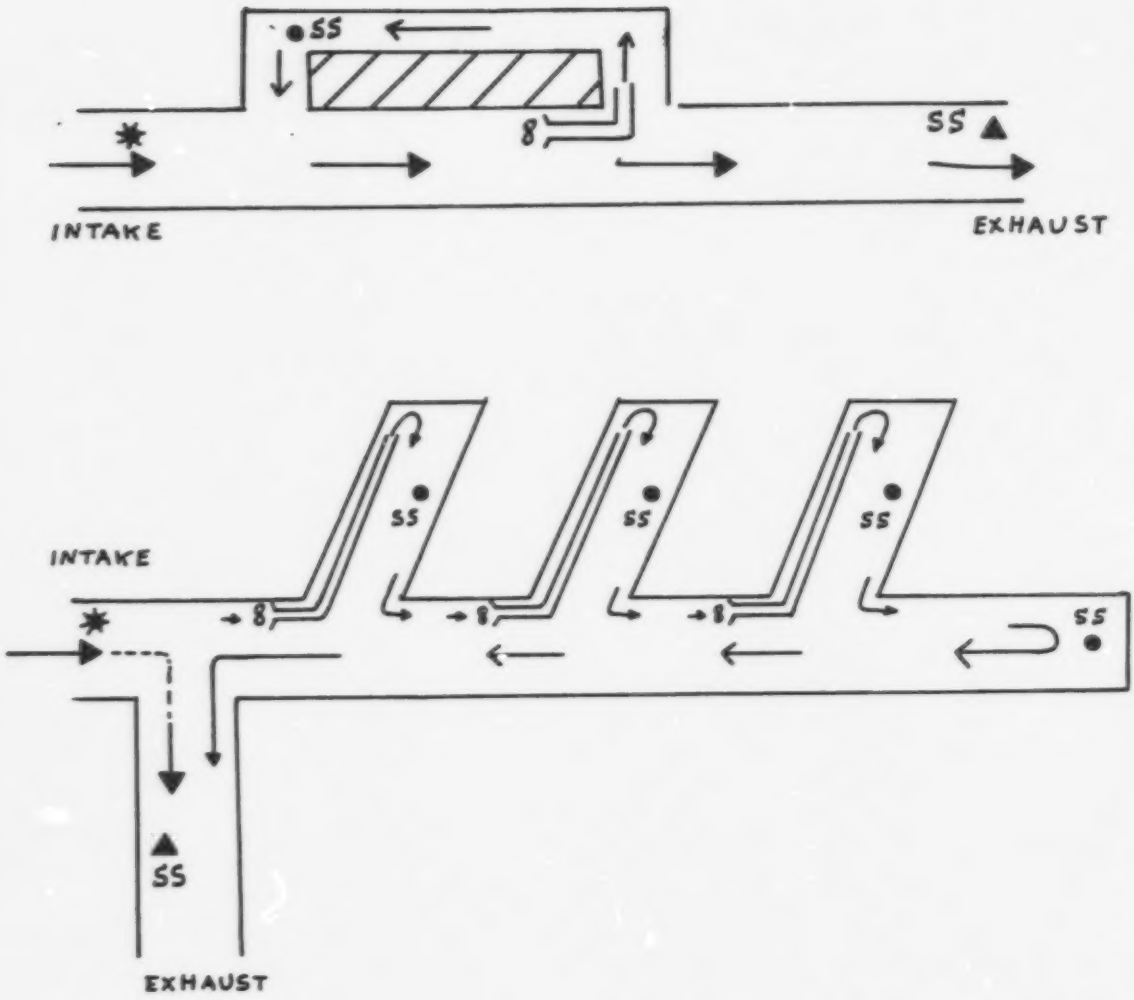


Fig. 6 - Experimental layout of some simple ventilation situations with recirculation. The asterisks are used to indicate tracer gas injection points. The solid circles and triangles indicate potentially useful sampling stations (SS).

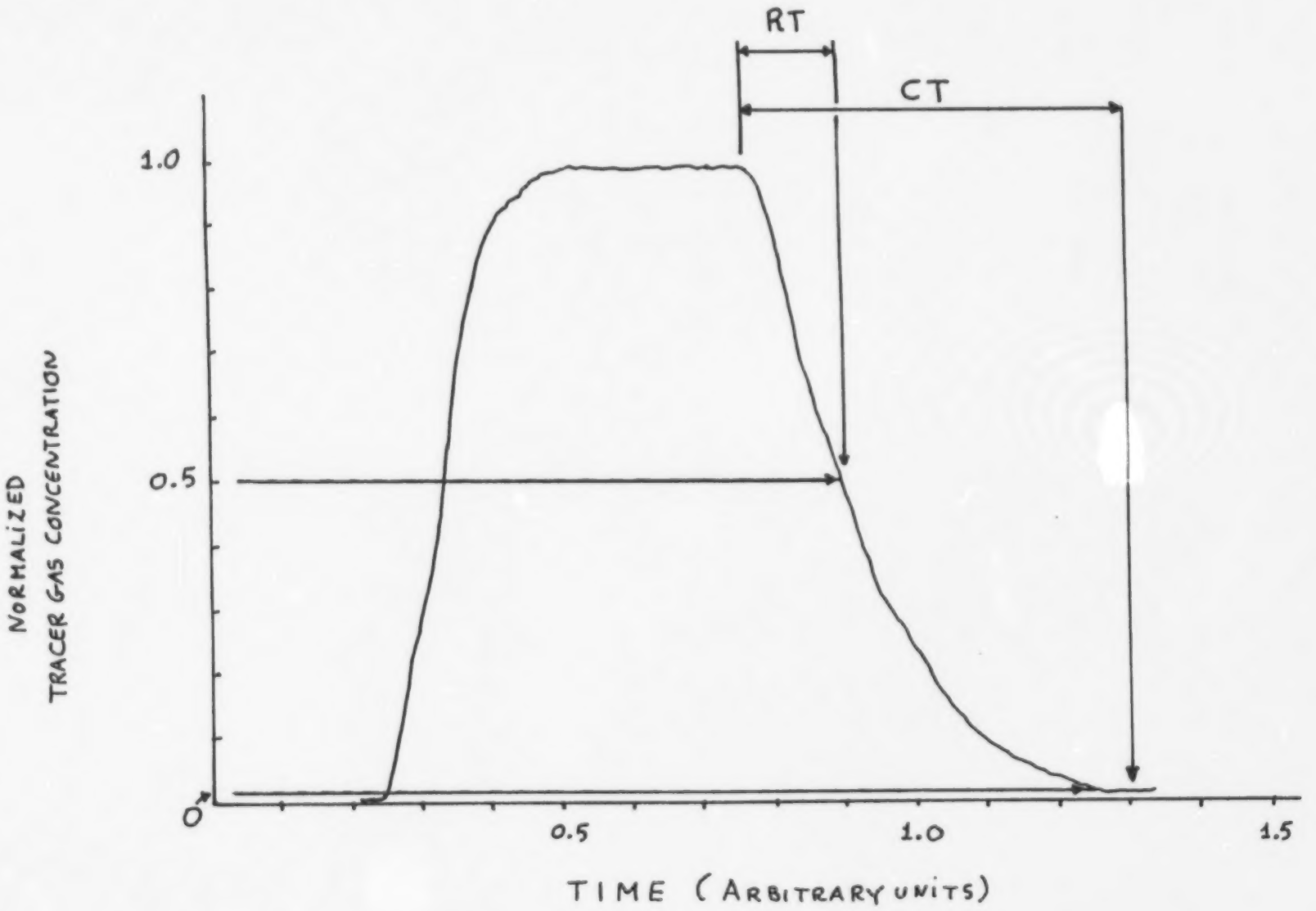


Fig. 7 - Tracer gas profile (concentration) versus time used to calculate residence time (RT) and clearance time (CT). (Continuous injection.)

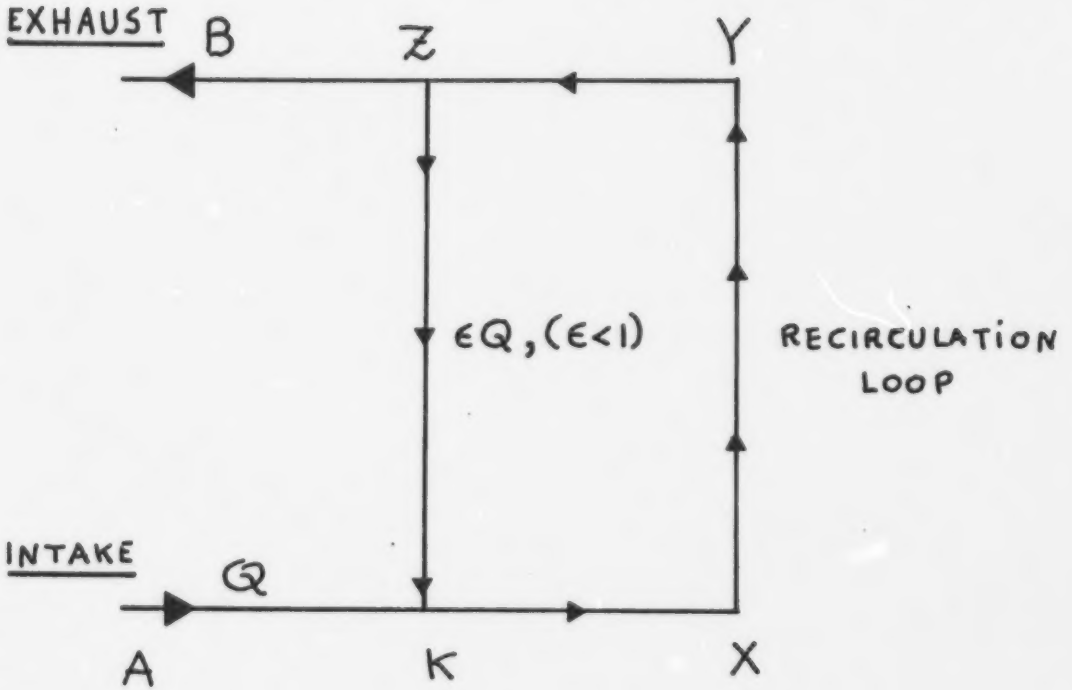


Fig. 8 - Simple recirculation circuit.

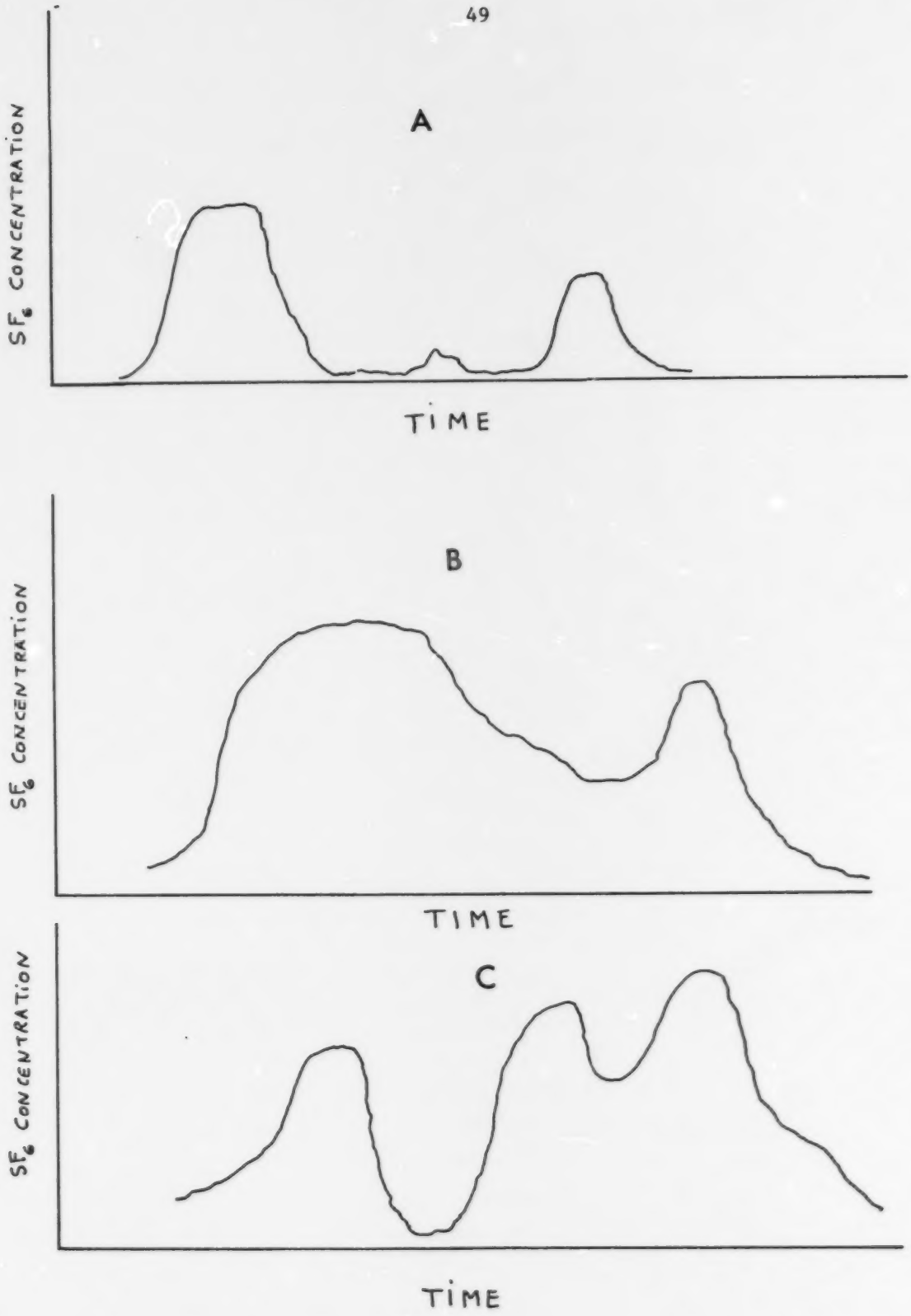


Fig. 9 - Tracer gas profiles for a simple ventilation, with recirculation, case (A) and more complex cases (B) and (C).

APPENDIX

INSTRUMENTATION USED FOR (CHEMICAL) TRACER GAS ANALYSIS IN VENTILATION STUDIES

There are a number of highly sensitive gas chromatographs (GCs) available in the market which makes them more than adequate for tracer gas work in ventilation studies. This discussion, however, will be limited to SF_6 and CFCs, gaseous chemical compounds which are ideally suitable for studying the ventilation characteristics of complex ventilation networks under difficult experimental conditions. Gas chromatographs for these types of compounds use electron capture detectors.

Gas chromatographs can be divided into two main classes, namely, laboratory-based GCs, and field portable GCs. There are distinct advantages in carrying out in situ measurements. These types of measurements require field portable instrumentation. There are only a handful of field portable gas chromatographs equipped with electron capture detectors. One such instrument, manufactured by SENSEX Sensing Technology Inc., (U.S.A.), and known under the commercial name SCENTOGRAPH is described below. This field portable GC will be used in the field surveys to be conducted in an underground uranium mine in conjunction with radon (thoron), and their progeny, studies.

DESCRIPTION OF THE INSTRUMENT

The SCENTOGRAPH is a portable gas chromatograph designed specifically to complete an entire analysis without the need for additional equipment usually required for interpretation of the results.

Computer controlled, the SCENTOGRAPH performs automatically the following functions:

- sample concentration
- sample injection
- chromatographic separation and detection
- peak identification and integration
- automatic calibration of up to 16 compounds
- front panel chromatographic display
- name, concentration level, retention time printout of up to 16 compounds
- automatic, unattended, repeating analysis
- automatic recalibration at preselected frequency
- TWA (Time Weighted Average) calculation.

The SCENTOGRAPH performs these functions in two operating modes:

a) Calibration - in which the SCENTOGRAPH uses an internal or external calibration mixture for analysis. At the end of this mode, the SCENTOGRAPH prints the name, concentration level, and retention time of each compound in the calibration mixture.

b) Analysis - in which the SCENTOGRAPH uses an ambient air sample for analysis. At the end of this mode, the SCENTOGRAPH prints the names, concentration levels and retention times of the compounds in the atmosphere which match the compounds identified during the calibration mode.

Since both modes are operated under the same conditions, and the calibration can be activated as frequently as required, the results obtained by the SCENTOGRAPH are claimed by the manufacturer to be highly reliable and accurate.

In addition, since the operation of the SCENTOGRAPH requires the handling of only two switches, at most, with the results automatically displayed, the instrument can be easily operated by any person after a short training period.

The SCENTOGRAPH is completely self-contained and will operate on its own gas supply for a minimum of eight hours. Moreover, the instrument can function unattended, perform analysis periodically, and calibrate itself at a chosen frequency with results printed for the entire period.

The functions and analysis carried out by the SCENTOGRAPH are controlled by a computer, Toshiba Model T1100 Plus.

SYSTEM DESCRIPTION

The SCENTOGRAPH consists of the following components or systems:

1. Gas Chromatograph Module

This module includes the column, the oven and the detector module. Columns, 1/8" to 12' in length, are replaceable. The column is heated by an oven whose temperature can be adjusted up to 130°C. The oven is well insulated and equipped with two separate heating zones. The first controls the temperature of the column: the second maintains the temperature of the detector. During normal operation the temperature of the detector is several degrees higher than that of the column.

The SCENTOGRAPH is equipped with two detector modules:

i) Argon Ionization Detector

ii) Electron Capture Detector

Changing from one detector to the other requires only the change of electronic switches. No hardware changes are necessary.

2. Preconcentrator/Sampling Loop

The instrument is coupled with a preconcentrator packed with a preselected adsorbant for obtaining ultra high sensitivities. If desired, a sampling loop for regular sampling of a required volume can be substituted.

3. Carrier Gas Cylinder

This internal cylinder contains Argon for the Argon Ionization/Electron Capture Detector. The carrier gas lasts about sixteen hours and the

cylinder is easily refilled.

4. Calibration Gas Cylinder

This internal cylinder contains the calibration mixture as preselected by the operator. The calibration cylinder is easily refillable, and, when filled, will provide a minimum of eight hours operation. Up to 16 compounds can be mixed in the calibration cylinder at any one time.

5. Printer Circuit Boards

There are three printed circuit boards, namely:

i) Date Processing Board

ii) Printer Board

iii) Electrometer Board.

6. Batteries

Two rechargeable lead-acid, 12 volt, 6A batteries are used. The batteries must be recharged after four to six hours of continuous operation or when the SCENTOGRAPH is not in use.

7. Computer

A personal (portable) computer, Toshiba model T1100 Plus, is incorporated in the metal case containing the gas chromatograph. The computer controls the operation of the instrument and processes and displays the data. An external strip chart recorder or printer can be interfaced with the computer to obtain a hard copy of the data. The instrument used by the Elliot Lake Laboratory has both capabilities.

METHODS OF CALIBRATION

Calibration of the SCENTOGRAPH can be carried out in two ways:

a) Direct calibration method; and

b) Computerized calibration method.

1. The Direct Calibration Method

The Direct Calibration Method is based on calibration for each preselected compound using a standard of each, having certified concentration level. If for example, a 2 ppm concentration level of benzene must be monitored, a standard of benzene, certified to a concentration level between 1-10 ppm, should be inserted in the internal calibration cylinder of the instrument. A maximum of sixteen certified standards may be mixed in an inert medium (air or argon) and inserted in the internal calibration cylinder. When in the calibration mode, a sample from the internal cylinder will be injected automatically into the gas chromatographic column. The instrument will, automatically, record the retention time of each standard, will integrate the area under each chromatographic peak, and will assign the concentration value of each calibration standard to each peak area. The computer screen will display (and the printer will print) the name of the compound, its retention time, and its concentration value. During the analysis, the instrument will attempt to match incoming peaks to those obtained during calibration. The SCENTOGRAPH will integrate any peaks obtained. If the retention time of the peak obtained during analysis does not match the peak obtained during calibration, only the retention time of the unidentified compound will be printed. If, however, the retention time of an analysis peak matches one obtained during calibration, the instrument identifies the compound by name, and calculates its concentration level based on a comparison between the area recorded for this particular peak and the peak areas recorded during calibration. The relationship between peak areas will be printed in ppm/ppb levels.

This method may be used to identify a maximum of 16 different compounds. Accordingly, using the Direct Calibration Method, for any given compound

to be identified, a certified standard of each compound should be inserted into the internal calibration cylinder. This method of calibration is highly accurate and duplicates a laboratory gas chromatographic analysis.

2. Computerized Calibration Method

If certified standards for compounds under analysis are unavailable, or in the instance where compounds to be analyzed are unknown, a Computerized Calibration Method may be used. Generally, this method uses a certified standard of one compound as the calibration source and compares the samples obtained during analysis to the calibrant compound in the same manner described in the Direct Calibration Method. The procedure is as follows:

A list of various compounds which are separated on a particular column, and their relative retention times, should be prepared. This list may be prepared by using the instrument in the manner specified in the Direct Calibration Method with the exception that certified standards of each compound are unnecessary. Alternatively, a published list may be used. One compound should be selected as the master compound to which all other compounds are to be compared. Generally, for best results, the master compound chosen should be at the mid-point of the list. The value of each relative retention time should be entered into the instrument's program as a percentage of the retention time of the master compound. For example, if the master compound chosen is acrylonitrile, its retention time will be considered as 100%. When compounds with retention times higher or lower than acrylonitrile are entered into the instrument's program, their concentration levels should be expressed as a ratio between their retention time, as numerator, and the retention time of the master compound, as a denominator.

Prior to calibration, only the master compound should be introduced as a

calibration standard and its concentration level recorded. During calibration, its retention time will be recorded in the instrument's memory as 100%, the area under the peak will be measured, and that area will be assigned the concentration level as specified in the calibration standard. During analysis, the instrument will attempt to find compounds with retention times at those percentages of the master compound. If peaks are identified at those retention times, the name of the compound, its retention time, and the concentration level will be printed. The word 'estimated' will also be displayed and printed. This is done to distinguish this calibration procedure from the Direct Calibration Method. The concentration level for each compound will be given relative to the concentration level of the master compound in ppm/ppb values. The compound that will not be 'estimated' will be that of the master compound, if that compound is present during the analysis. Chromatographic peaks arriving at retention times different from those specified, will be printed as retention times, with no compound identification given.

FRONT PANEL CONTROLS AND DISPLAYS

The front panel has the following controls:

Switches

a) ON - This switch functions both to activate and deactivate the instrument;

b) Calibration (CAL) - This switch initiates CALIBRATION;

c) RUN - This switch initiates ANALYSIS; and

d) RE-SET - This switch will inhibit the chromatograph on the LCD and allow the operator to restart ANALYSIS or CALIBRATION. It must be pressed for ten (10) seconds.

2. Keyboard

The keyboard is used to alter the various parameters used during CALIBRATION and ANALYSIS. The parameters can be altered sequentially, in the sequence described below or individually, as required. The parameters are:

a) Backflush,

b) Analysis option (for direct or computerized calibration),

c) Sampling time (in seconds: 10 to 999),

d) Delay time (a maximum of 2 seconds),

e) Desorption time (a maximum of 4 seconds), and

f) Inhibit time (in seconds: 10 to 999).

3. Liquid Crystal Display (LCD)

An LCD indicates the following operational states:

a) Warming up,

b) Instrument Ready,

c) Sampling,

d) Processing,

e) Inhibit Active,

f) Enter Parameters (enter PARM),

g) Calibration,

h) Analysis, and

i) Chromatograph Display.

CHROMATOGRAPH PRINTER AND COMPUTER DISPLAY

The printer and display operate in two ways:

1. Parameters

The printer will print the parameters which are stored in the SCENTOGRAPH's memory. The parameters will be printed in the following sequence:

a) Date, hour, minute,

b) Sampling time,

c) Delay time,

d) Desorption time,

e) Inhibit time,

f) Parameters for each compound,

g) Autoanalysis rate,

h) Recalibration rate,

i) Oven temperature,

j) Chart duration rate,

k) TWA,

l) Alarm enable/disable,

m) Print option,

n) Backflush option, and

o) Analysis option.

2. Results

The printer will, also, print the results of CALIBRATION and ANALYSIS in the following sequence:

a) Identification or operation (CALIBRATION or ANALYSIS),

b) Date, hour, minute, and

c) For each compound: name, concentration level and retention time (estimated or actual).

Results will be printed and displayed, continuously, after each ANALYSIS or CALIBRATION. Alternatively, the display and printer will show results after an alarm threshold level is achieved and for Time Weighted Averages.

BACK PANEL CONTROLS

The back panel of the instrument has the following controls:

a) Carrier Gas Valve and Inlet. The inlet to the carrier gas cylinder and the valve to control its flow is located on the back panel of the instrument;

b) Calibration Gas Valve and Inlet. The inlet to the internal calibration gas cylinder and the valve to control its flow are located on the rear panel of the instrument;

c) Recorder Output;

d) Battery Input. A battery charger must be plugged to the instrument to recharge the internal batteries;

e) Sampling Pump Output. A small output tube on the back panel of the instrument will release that portion of the atmospheric sample that is unnecessary for analysis: and

f) RS 232 Output.

PRESSURE GAUGES

Three pressure gauges are located on the front panel of the instrument. These gauges indicate, respectively, the pressure of the calibration gas cylinder, the carrier gas cylinder and the column (carrier gas) pressure. Maximum pressure for each cylinder should not exceed 1.24×10^4 kPa (1800 psi). Normal column operating pressure is 138 to 207 kPa (20 to 30 psi).

INSTRUMENT OPERATION

To operate the instrument (SCENTOGRAPH), turn the power on. After a warm-up period the computer screen will display 'Instrument Ready'. At this point the instrument can be operated in two different modes, namely,

calibration and sample analysis. Pressing the key labelled CAL will initiate a calibration run. Pressing the key labelled RUN will initiate sample analysis. If analysis is initiated before calibration, a calibration will be automatically performed prior to analysis to update the computer system.

The computer display and printer print-out can show five different operations, namely: sampling, processing, inhibit active, calibration, and analysis.

a) If the display shows SAMPLING, the operation being performed is as follows: The sampling pump is automatically activated and the sampling valve opens. If the instrument is in the CALIBRATION mode, a sample will be drawn from the internal calibration cylinder or from a fixed calibration source. If the instrument is operating in the ANALYSIS mode, a sample will be drawn from the atmosphere. The display and print-out will automatically identify the mode of operation, date and time.

b) If the display shows PROCESSING, a delay valve opens for a pre-selected time and a heating filament is activated to heat the sample that has been collected in the preconcentrator.

c) If the display shows INHIBIT ACTIVE, the sample is being processed through the column and the instrument automatically eliminates undesirable injection peaks.

d) If the display shows CALIBRATION, the instrument operates as follows. The electronic signal from the detector during the calibration mode is sampled and averaged every 0.5 seconds. Each new average is compared to the previous one to determine the movement of the electronic signal. Noise interference will be automatically eliminated, and electronic gain change, as required, is automatically obtained. Peak integration starts when the electronic signal rises. With the first rise in the electronic signal the instrument will begin to count the area under the peak, i.e., a peak

integration will be initiated. The largest peak detection time for each compound is stored in the computer's memory in order to provide 'baseline' measurements.

e) If the display shows ANALYSIS the following instrument operation is carried out. During analysis, the area under each peak is counted as indicated above, and the highest value for each peak is compared to the range for each peak obtained during calibation. If the values match, the identity of the peak is established. Analysis ends when the last peak has been detected and identified.

In addition to the automatic operation, the instrument can be operated on the manual mode. In this case the instrument will follow the operational sequence as described above except that ANALYSIS or CALIBRATION must be initiated manually by pressing RUN or CAL, respectively.

Operational procedures are greatly simplified if the tracer gas (i.e., chemical compound) to be detected is already known, e.g., SF_6 injected in mine air, because in this case compound identification is not required.

There are other capabilities and possibilities of the instrument too lengthy to describe here. The interested reader should refer to the Instruction Manual for more detail.